CODIGEM

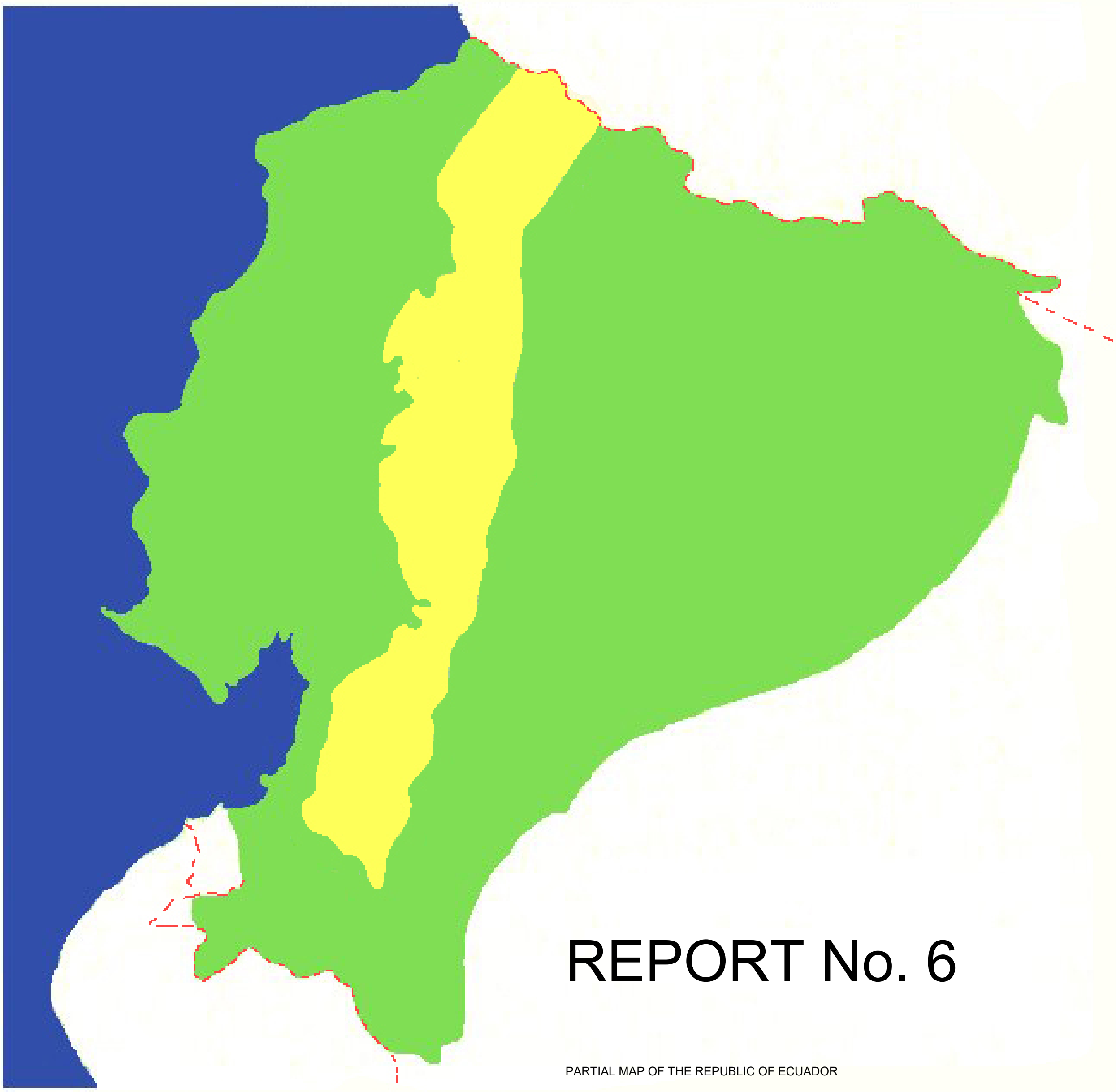
CORPORACIÓN DE DESARROLLO E INVESTIGACIÓN GEOLÓGICO-MINERO-METALÚRGICA

MINISTERIO DE ENERGÍA Y MINAS

DFID

DEPARTMENT FOR INTERNATIONAL DEVELOPMENT

BRITISH GEOLOGICAL SURVEY



REPORT No. 6

PARTIAL MAP OF THE REPUBLIC OF ECUADOR

WORLD BANK MINING DEVELOPMENT AND ENVIRONMENTAL CONTROL PROJECT

GEOLOGICAL INFORMATION MAPPING PROGRAMME (WESTERN CORDILLERA)

PATRI MATRIQUE

MINING DEVELOPMENT AND ENVIRONMENTAL CONTROL PROJECT

GEOLOGICAL INFORMATION MAPPING PROGRAMME

Report Number 6

CONTROL OF QUALITY OF GEOCHEMICAL DATA

P. N. Dunkley

A. Gaibor C.

CODIGEM-BRITISH GEOLOGICAL SURVEY

Quito-Ecuador

1997

Stalyn Paucar

2024 edition

Reference

Dunkley, P. & Gaibor, A. (1997). *Control of Quality of Geochemical Data* (Stalyn Paucar, Ed., 2024). Report Number 6. Geological Information Mapping Programme. BGS-CODIGEM/MEM.

CONTENTS

FIGURES

TABLES

APPENDICES

1. INTRODUCTION

This report describes the methods used to assess and monitor the quality of stream sediment geochemical analyses from the first year of the Geological Information Mapping Programme (GIMP).

Based on this assessment, recommendations are made for monitoring the quality of analyses for the remainder of the geochemical survey.

1.1 Sample collection

The sampling method is described in detail in a report by Dunkley et al. (1997), and conforms to the procedures given in section 12.5.1.4 of the final report of IGCP Project 259 (Darnley et al., 1995). In brief, active stream sediments are wet-sieved in the field and the 80 mesh (177μm) collected for analysis. An important feature of the method is that the loss of fine material by excessive washing is avoided by using a limited amount of water when sieving, which is recycled and finally left to stand for 20 minutes to allow all but the very finest particles to settle prior to collection. The samples are then collected as a slurry of sediment and water in pre-numbered Kraft sample bags.

1.2 Sample preparation

On return from the field the samples are initially left to stand for several hours (usually over night) to allow the fine particles to settle before decanting off the excess water. They are then dried under ambient conditions (sun and air) in their original bags.

On return to the office the samples are desegregated by hand using ceramic pestles and mortars. This is to break down any aggregated grains and clayey lumps which form during the drying process, to produce a fine homogenous sample for analysis. It is important at this stage not to overgrind the samples. The samples are then split by cone and quartering and 50 gram aliquots are sent to the laboratory in new Kraft sample bags. The residual samples are returned to their original sample bags for storage.

1.3 Sample numbering system

The sample numbers used in the field are in random order. At the beginning of the project 3000 sample bags were numbered sequentially (from 1 to 3000) and then thoroughly shuffled. Sample teams were provided with the randomized sample bags in batches of 50. In the second year of the project a further 7000 bags were numbered and mixed to bring the total number to 10000.

The samples are submitted for chemical analyses in batches of 120. Prior to submission they are placed in numerical order. In this manner, consecutive samples within each analytical batch originate from widely dispersed locations and from different sample teams. Through this randomization process any systematic between-batch variation in the chemical analyses (produced by errors in the laboratory) is transformed into increased analytical variability and hence increases background noise across the area. Conversely, without randomization, between-batch analytical variation would result in differences in background levels between the areas from which each batch of samples would have originated.

1.4 Chemical analysis

The samples are sent to Bondar Clegg in Vancouver for analysis using the following methods:

Au by fire assay and atomic absorption spectrometry.

Aqua regia digestion (HCl + HNO_3, 3:1) followed by:

Analysis of Ag, Cu, Pb, Zn, Mo, Ni, Co, Cd, Bi, As, Sb, Fe, Mn, Te, Ba, Cr, V, Sn, W, La, Al, Mg, Ca, Na, K, Sr, Y, Ga, Li, Nb, Sc, Ta, Ti and Zr by inductively coupled plasma-atomic emission spectrometry.

Analysis of As and Sb in the same solution by hydride generation and determination by atomic absorption spectrometry.

Analysis of Hg in the same solution by cold vapour generation and determination by atomic absorption spectrometry.

For Au analysis by fire assay, it is standard practice to analyse 30 gram samples. During the first year of the project however, 20 gram aliquots were analysed because it was uncertain whether sufficient samples could be collected in some areas for a 30 gram assay, bearing in mind that the laboratory required enough material for a duplicate analysis and that it was also desirable to retain some residual samples for archiving. In hindsight this proved to be well-founded, because insufficient samples were obtained at many sites for a duplicate 30 gram assay. However, due to the inherent difficulties in obtaining representative samples for gold analysis, because of nugget effects, a larger aliquot would have been preferable. In the second year of the sampling programme more than sufficient samples were obtained at most sites, and therefore the analytical scheme was changed to analyse 30 gram aliquots for Au.

2. DEFINITIONS

When a finely divided geochemical sample is analysed repeatedly using a fixed procedure, variable results are obtained for the concentration of the analyte. This variation is caused by a combination of all the small errors that are introduced at every stage of the procedure, including errors in weighing, dissolving, measuring volume and instrumentation.

Analytical error usually has a Normal distribution (Thompson, 1983). Thus, the variability of the analyses can be described by the two parameters of the probability distribution, namely the mean and the standard deviation.

The central tendency of the results is estimated by the arithmetic mean ($\bar{x}$) given by the formula:

$$\bar{x} = \sum \frac{x_i}{n}$$

Where x_i are the successive values of the n observations.

The spread of results is quantified by the estimated standard deviation (s) given by the formula:

$$s = \sqrt{\frac{\sum(\bar{x} - x_i)^2}{n-1}}$$

Based on the Normal probability distribution it is possible to estimate the proportion of values that should fall within certain ranges, expressed in terms of standard deviation units above and below the mean. Using these parameters, which can be obtained from standard statistical tables, confidence boundaries can be defined for an analytical result. Table 1 gives the proportion of values that should fall within commonly used ranges of standard deviation units. For example, 95% of the values should fall within the range $\bar{x} \pm 1.96s$ and an average of only 5% should fall outside this range.

Table 1. The proportion of observations falling within ranges of the Normal distribution expressed as standard deviation about the mean. (Taken from Thompson, 1983)

Range	Proportion
$\bar{x} \pm s$	68.26 %
$\bar{x} \pm 1.96s$	95.00 %
$\bar{x} \pm 2s$	95.46 %
$\bar{x} \pm 3s$	99.74 %

In geochemistry the term *accuracy* is used to denote how close an analytical result is to the true concentration of the analyte, and the term *bias* for the difference between the analytical result and the true concentration. In reality, the true value cannot be ascertained. Only an estimation of the true value can be made, by using a variety of analytical methods based upon different physical principles, each of which is given a weighting appropriate to the limitations of the method. For this reason, the analytical results of geochemical reference samples should be expressed as *acceptable* or *preferred* values rather than as true values.

Precision is a measure of how repeatable and comparable a result is. For a given element in a given sample, an analytical method with good precision should produce a smaller range of analytical results than a method with poor precision.

Precision in geochemistry is usually defined as:

$$p = \frac{(2s)}{\bar{x}} * 100\% \qquad (1)$$

In other words, the range relative to the concentration, in which approximately 95% (actually 95.46%) of the analyses should fall (see table 1).

Precision quoted in this manner is therefore related to a specific concentration. Precision, however, varies with concentration, generally improving with increased concentration, as shown in Figure 1. Values of precision should therefore be qualified by the concentration at which they have been measured. For example, in Appendix 1, the precision for copper obtained by replicate analyses of the J-1 reference sample is 15.14% at 181.4 ppm, whereas that for the COR-1 reference sample is 36.02% at 20.7 ppm (the concentrations being the mean concentrations of the replicate analyses).

Good precision does not necessarily mean good accuracy. In geochemical exploration it is very important to obtain and maintain the best possible precision, so that the analyses of samples collected from widely spaced sites over prolonged periods of time can be compared. Nevertheless, it is still important in exploration geochemistry to have a check on accuracy so that results obtained from different surveys or perhaps by different methods of analyses may be compared.

Detection limit is the lowest concentration that can be estimated from a single analysis. IUPAC (1978) defines detection limit as the concentration of the analyte that corresponds to a response level equal to the mean blank reading plus three standard deviations. However, the definition does not fully define a blank. For example, instrumental detection limits may be obtained by the repeated analysis of a blank solution (a pure solution not containing a dissolved sample) over the shortest possible time interval. This provides the lowest possible detection limit, but does not take into account matrix effects, such as inter-element interferences, which occur in the analysis of real samples. Realistic detection limits may be obtained by the replicate analysis of a series of samples under normal conditions. The standard deviations of the replicate analyses for each sample are then extrapolated graphically or by regression to obtain an estimate of the standard deviation at zero concentration (s_0). An estimate of the detection limit of the system is then given by $3s_0$. This value is typically 4 to 20 times greater than the instrumental detection limit (Thompson, 1988).

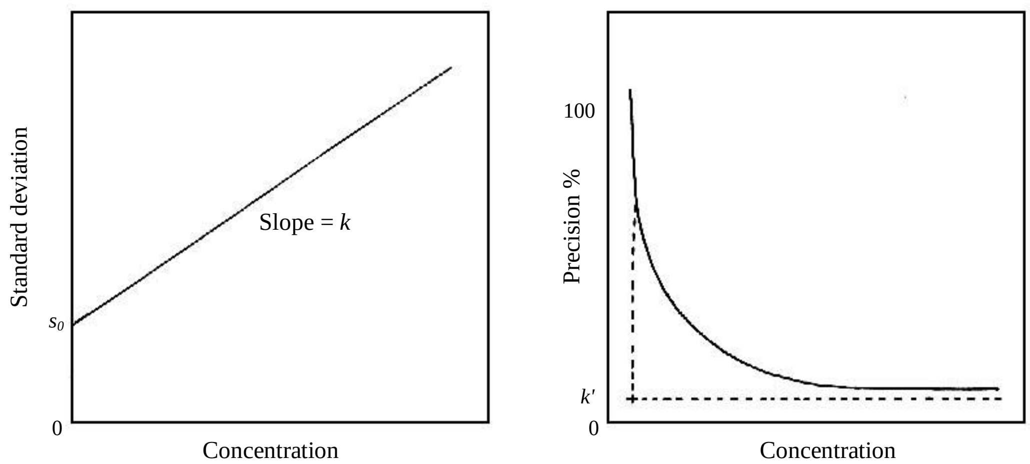


Figure 1. Concentration vs. Standard deviation (left) and Concentration vs. Precision% (right)

3. METHODS OF QUALITY CONTROL USED BY THE GIMP

The quality of analyses in the GIMP has been assessed and controlled by several different methods. These include the routine analyses of reference samples, and the analysis of samples in duplicate.

3.1 Use of reference samples

The quality of chemical analyses can be monitored using reference samples. Such reference samples are prepared in relatively large quantities and subsamples are submitted routinely with each analytical batch of samples in order to monitor precision. The reference samples are also analyzed by other laboratories in order to gain an idea of the accuracy of the results obtained from the routine laboratory.

Prior to commencing the analytical programme of the GIMP, three reference stream sediment samples were collected and prepared in large quantities (15-20 kg each). One sample, J-1, was collected from the R. Junín. It contains weakly to moderately anomalous concentrations of some of the elements of interest to mineral exploration (Cu, As, Sb, Hg). Another sample, COR-1, was collected from the R. Angamarca near El Corazón and contains low concentrations of these elements. Portions of these two samples were also mixed together to form a third reference sample (M-1) of intermediate composition. The three reference samples were split into 50 gram aliquots by a combination of riffling and cone-and-quartering. Two hundred splits of each reference sample were prepared and stored in Kraft sample bags. Two splits of each of the three reference samples were included in each batch of 120 samples sent to the laboratory. These have exactly the same appearance as the routine samples and therefore cannot be recognised as reference samples by the laboratory.

During the course of the first year of the analytical programme each reference sample was analyzed 30 times. The means and standard deviations of the replicate analyses for each element were calculated for each reference sample. Values falling outside the limits of $\bar{x} \pm 3s$ were rejected as possibly spurious, resulting from non-systematic or gross errors, and the mean and standard deviations recalculated.

The results and statistical analyses of the reference samples are given in Appendix 1. The mean results ($\bar{x}$) are taken as the acceptable values for these samples. Concentrations of several of the elements are below the detection limits quoted by Bondar Clegg (e.g. Ag, Cd, etc.). Unfortunately, the actual values obtained below detection are not reported by the laboratory, but are simply quoted as below detection limits, when in practice actual values are obtained by the laboratory which include negative values (i.e. a value below 0). For some elements within the reference samples the concentrations are well below the laboratory detection limit. For other elements the concentrations are close to detection and a large proportion of the values are quoted as below detection. In such cases it is not possible to calculate the mean concentrations of these elements in the reference samples. In cases where an element occurs in low concentration but the large majority of the analytical results are above the laboratory detection limit, with only a few quoted below the limit, those values below detection were reset to 2/3 the quoted laboratory detection limit prior to calculation of the mean value.

The three reference samples (J-1, M-1 and COR-1) were also analyzed at the laboratories of the British Geological Survey (BGS), in order to provide an inter-laboratory check. Here they were analyzed by comparable but not identical methods to those used by Bondar Clegg. These consisted of aqua regia digestion followed by a combination of ICP-AES and ICP-MS for all the elements, except Hg which was determined by atomic fluorescence spectroscopy. The results for the majority of the trace elements compare very well between the two laboratories (see Appendix 1). For some of the major elements the results from BGS are higher than those from Bondar Clegg. This is probably due to differences in the actual method of aqua regia digestion between the two laboratories; BGS used a method which involved refluxion of the acid, which probably results in more complete digestion. As a check, BGS also analyzed the major elements by XRF, which being a method of total analysis gave higher results than the wet chemical techniques.

Four reference samples from BGS (S14, S15, S24 and S3B) were also submitted to Bondar Clegg under the guise of routine samples. The analyses of these standards for selected elements are presented in Appendix 1 together with average values of replicate analyses obtained at BGS using XRF for comparison. For Cu, Zn and As there is very good agreement between the two sets of results. For other elements there is a reasonable comparison, although the XRF results are higher (e.g. for Pb and Ni). This is because XRF produces a total analysis including metals held in silicate minerals.

In order to monitor batch precision and accuracy the analyses of each of the three reference samples J-1, M-1 and COR-1 are presented on control charts, in which concentration is plotted against sample batch number (Appendix 2). Lines representing the mean plus and minus standard deviation intervals are also shown on these charts. From consideration of the Normal distribution, it can be expected that only about 5% of the individual results should fall outside the limits $\bar{x} \pm 2s$ and only 0.3% outside $\bar{x} \pm 3s$. With the analysis of each batch of samples, the results of the reference samples are plotted on the charts. The charts provide a rapid visual method for monitoring within-batch and between-batch precision and accuracy. Should, for example, an unacceptable proportion of results for a given batch fall outside these limits, this would indicate a departure from the control and the batch of samples should be reanalyzed. The charts should also indicate any long-term systematic drift or periodic variation in analyses, which would need to be rectified by discussion with the laboratory.

As more analyses of reference samples become available, the mean and standard deviations should be recalculated and the control charts reconstructed. Any major change in acceptable value should be investigated.

For some elements used in mineral exploration, the reference samples do not have suitable concentration ranges (see Appendices 1 and 2). In addition, therefore, a number of the routine samples which were found to have high concentrations of these elements were resubmitted for replicate analyses. There was insufficient material to produce a large number of analyses, but 5 or 6 replicate analyses were obtained for each of these samples. These analyses are presented in Appendix 1 and provide a measure of precision for a number of elements which occur below the detection in the three main reference samples.

In the second year of the project a number of new reference samples were prepared (PE-1, CN-1 and M-2) for monitoring precision. These have moderately high to high concentrations of the elements of most interest to mineral exploration and pollution studies (Au, Ag, Cu, Pb, Zn, Cd, Hg, Bi, W, Mo, As, Sb and Hg). The analyses of these reference samples will be reported in due course when more results are available.

Bondar Clegg also reports analyses of its own laboratory reference samples that are routinely analyzed with each batch of samples. These data are presented in Appendix 1.

3.2 The use of duplicate analyses for monitoring precision

The quality of chemical analyses may be assessed by duplicate analyses. At the end of the analytical programme of the first year of the project 91 samples (approximately 8% of the total number) were resubmitted for reanalysis. These were selected partly at random and also chosen to include samples with anomalous values from the first round of analyses.

The quality of the analysis may be assessed rapidly and qualitatively by plotting the original analytical values against the duplicate values on a scatter plot. Ideally, the two groups of analyses should plot as a straight line with a gradient of 45°, with a restricted scatter about this trend. Good analytical precision results in a close scatter of the points about the trend. Bias in the analyses, due to systematic errors or differences in the two methods of analyses, produces trends that deviate from the 45° line. Scatter plots of the original analyses and duplicated analyses are presented in Appendix 3. For all of the elements these produce trends of approximately 45° indicating no systematic bias between analytical batches. For some elements there is a large scatter of points about the trend at lower concentrations, reflecting generally poorer precision at lower concentrations.

As previously stated, a single standard deviation (for example of a reference sample) cannot describe the precision over a range of concentrations, because precision varies with concentration. An equation or plot relating standard deviation to concentration is therefore more appropriate. Thompson and Howarth (1976, 1978) describe two methods of assessing precision over a range of concentrations by means of duplicate analyses. Both of these methods have been employed by the GIMP and are described below.

3.2.1 Method 1 of Thompson and Howarth

In the first method, where more than 50 duplicate analyses are available, the variation of standard deviation of the determination (s_c) can be related to the concentration (c) by the linear function:

$$s_c = s_0 + k * c \qquad (2)$$

where s_0 is the standard deviation at zero concentration and k is the gradient of the straight line:

Equations 1 and 2 can be combined to give:

$$p * c = 2s_0 + 2k * c$$

or

$$p = \frac{2s_0}{c} + 2k \qquad (3)$$

Thus, at concentrations well above the detection limit, precision can be estimated from $2k$, as $\frac{2s_0}{c}$ will be very small.

If there are sufficient analyses at low concentrations the practical detection limit c_d (when $p = 1.0$) can also be estimated from the expression:

$$c_d = \frac{2s_0}{(1 - 2k)} \qquad (4)$$

The precision characteristics of an analytical system can thus be estimated.

The procedure for estimating precision from duplicate analyses is described in detail by Thompson and Howarth (1978). For 50 or more duplicate analyses the procedure is as follows:

From the corresponding pairs of analyses (x_i, y_i) the mean $\frac{x_i+y_i}{2}$ and the absolute difference $|x_i - y_i|$ are calculated.

The results are arranged in increasing order of the mean results, maintaining the correspondence between the means and the differences.

From the first 11 pairs the mean of the means is calculated and the median of the differences selected.

This procedure is repeated for each group of 11 results, ignoring any remainder less than 11.

A linear regression of the medians on the means is performed to obtain the intercept and gradient, which are respectively estimates of s_0 and k as defined above.

Examples of graphs based on this method for 91 duplicate analyses are presented in Appendix 4. Regression of the medians on the means was used to obtain estimates of s_0 and k which are summarised in Appendix 4.

3.2.2 Method 2 of Thompson and Howarth

Thompson and Howarth (1978) also present a graphical method for estimating precision from duplicate analyses, where there are 50 or fewer duplicates; the method however may be used for checking the precision of any number of duplicate analyses.

A precision control chart based on equation 2 is constructed for a specified level of precision. Lines of the 90th and 99th percentiles are plotted to define fields in which respectively 90% and 99% of the duplicate analyses should plot if the specified level of precision is achieved.

In this method the precision required is specified in the form:

$$s_c = s_0 + k * c$$

For example, for a required precision of 10% (p = 0.1), k from equation 3 will be 0.05 at high concentration. The specification for 10% precision would therefore be:

$$s_c = s_0 + 0.05 * c$$

For a given detection limit (c_d), s_0 can be calculated from equation 4. For example, if a detection limit of 5 units is specified, then substituting in equation 4.

$$s_0 = \frac{5(1-0.1)}{2} = 2.25$$

The percentile lines d_{90} and d_{99} are obtained from the following equations:

$$s_c = \frac{d_{90}}{2.326}$$

$$s_c = \frac{d_{99}}{3.643}$$

or

$$d_{90} = 2.326\ (s_0 + k * c) \qquad (5)$$

$$d_{99} = 3.643\ (s_0 + k * c) \qquad (6)$$

The percentile lines can be plotted over a suitable range of concentrations (c) to form the control chart.

From the corresponding pairs of analyses (x_i, y_i) the mean $\frac{x_i+y_i}{2}$ and the absolute difference $|x_i - y_i|$ are calculated and plotted on the control chart. If the concentration range is greater than one logarithmic cycle it is best to plot the control chart on log-log scales, otherwise arithmetic scales can be used.

Thompson and Howarth (1978) do not define the factors in equations 5 and 6. They are assumed to be factors that relate the standard deviation (s_c) to the differences between duplicate analyses at the specified percentile levels. Thompson and Howarth describe the resulting lines d_{90} and d_{99} respectively as the 90th and 99th percentiles of the absolute difference between duplicates as a function of concentration, assuming a normal distribution of error. If the duplicate analytical data comply with the specified precision and detection level, then on average 90% of the points will fall below the d_{90} line and 99% below the d_{99} line. If the precision is better, a higher proportion of the points will tend to fall below the lines. If it is worse, the opposite will tend to occur.

An example of this type of control chart is given in Figure 2.

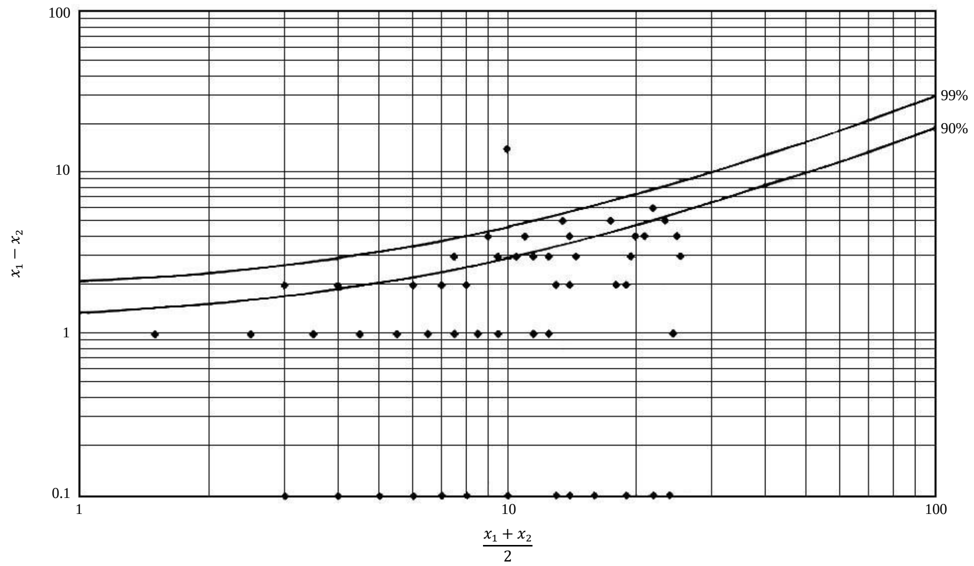


Figure 2. Lithium duplicate analyses control chart (see Appendix 4)

The duplicate analyses from the GIMP are plotted on the control charts presented in Appendix 4. These indicate that each element has a different precision, the level of which was obtained empirically. For each element the 90th and 99th percentiles were plotted for various levels of precision, in order to empirically ascertain the level that most closely describes the data. The selection of the detection limits used in the equations for the percentile lines is described in the Section 3.3.

The duplicate analyses indicate that it would be unrealistic to expect a precision of 10%, which is often taken arbitrarily as an acceptable level for geochemical exploration. For some elements precision is better than 10%, but in general it appears to be in the range 10-20%, and for a few elements at lower concentrations it appears to be considerably poorer. A more pragmatic approach therefore, would be to accept the levels of precision derived empirically from the duplicate analyses of the first year of the project, and expect that future analyses should at least maintain these levels.

3.2.3 Precision attained for each element

A brief summary of the precision attained for each element is given in the following paragraphs.

Antimony is determined by hydride generation – AAS gives good precision. For a precision of 10% only one duplicate analysis plots above the 99 percentile line, and less than 5% of the analysis is above the 90 percentile line. Precision therefore appears to be slightly better than 10%.

Arsenic is determined by hydride generation – AAS gives very good precision. All but a single duplicate analysis plots below the 99 percentile lines for a precision of 5%.

Barium analyses appear to have a precision of about 20%. Although three out of the 91 analyses plot above the 99 percentile line at a precision of 20% only six points (approximately 6% of the analyses) plot above the 90 percentile line.

Cadmium has a precision of about 15%. Approximately 90% of the analyses fall below the 90 percentile line for a precision of 15%.

Chromium has a precision which is probably better than 10%. Only three duplicate analyses (about 3 percent of the analyses) plot above the 90 percentile line as defined for a precision of 10%.

Cobalt has a precision of about 15% or slightly better. More than 90% of the duplicate analyses plot below the 90 percentile line as defined for a precision of 15%.

Copper shows a classic pattern of variable precision with concentration. Overall, the analyses show a precision of about 20%. For concentrations up to about 100 ppm the precision is relatively poor. However, at concentrations above about 100 ppm the duplicate analyses plot well below the 99 and 90 percentile lines, indicating much better precision than 20%. At these higher concentrations the precision is between 10 and 15%. It may therefore be concluded that although it would be desirable to attain a better overall precision, at anomalous levels (>100 ppm) the analyses have good precision.

Iron analyses have a precision of about 15% or slightly better. For this level of precision more than 90% of the duplicate analyses fall below 90 percentile line.

Lead has very poor precision. Overall, the 91 duplicate analyses have a precision of about 40%, although, as with copper, at higher concentrations the precision improves. Above about 40 ppm the precision for lead appears to be about 20% or better. This implies that at anomalous levels the quality of the analyses is reasonably reliable.

Lithium shows an analytical precision of about 15% with approximately 90% of the duplicate analyses falling below the 90 percentile line. The lithium control chart in Appendix 4 may appear to have less than 91 points, but this is because many points plot in exactly the same position.

Manganese shows an analytical precision of between 10% and 15%. For practical purposes future analyses should maintain a precision of at least 15% or better.

Mercury shows unusual variation in precision with better precision at low concentrations than at high concentrations. Above about 2 ppm there are a number of points which indicate very poor precision. At concentrations below a few ppm analytical precision is significantly better. Two different control charts for mercury are presented in Appendix 4 for various levels of precision and detection limits. If a detection limit of 0.04 ppm is accepted, then below about 2 ppm the analyses have a precision of about 15% or slightly better.

Molybdenum also shows variable precision with concentration. The control chart in Appendix 4 appears to have few points, but this is because many of the analyses at low levels and those below the laboratory detection level (as quoted by Bondar Clegg) plot in the same positions. Precision is approximately 25% overall, with slightly over 10% of the duplicate analyses plotting above the 90 percentile line, most of which have concentrations below 10 ppm.

Nickel analyses have a precision of about 10%. Slightly more than 10% of the analyses (10 out of 91) plot above the 90 percentile line for a precision of 10%.

Silver analyses show poor precision of approximately 25%.

Strontium shows a precision of about 25%, with slightly more than 90% of the duplicate analyses falling below the 90 percentile line.

Vanadium shows a precision of between 20% and 25%.

Zinc shows a precision of 20%.

3.3 Estimation of practical detection limits

The detection limits quoted by laboratories are often obtained by replicate analyses under ideal conditions using standard solutions composed of pure chemicals, and are usually considerably more optimistic than those that are actually achieved in practice for solutions containing actual samples. It is therefore important to estimate the practical limits of detection for the system in actual use.

A realistic method of obtaining practical detection limits is to analyze in replicate a series of reference samples over a range of concentrations and obtain the mean concentration and standard deviation for each sample. The standard deviation is then plotted graphically against the mean concentration and by extrapolation or regression the standard deviation at zero concentration (s_0) is obtained. By convention, the detection limit is then calculated as $3s_0$ (IUPAC, 1978). Alternatively, s_0 can be estimated from duplicated analyses using the method of Thompson and Howarth (1978) which is described in the previous section of this report (Method 1).

Both methods of calculating detection limits were applied. The method of Thompson and Howarth using duplicate analyses appears to be unreliable. For several elements unrealistically high detection limits were obtained (e.g. Cu 11 ppm, Zn 15 ppm, and Pb 12 ppm) and for others (Mn, Sr and Hg) negative detection limits. The graphical plots using this method to estimate s_0 are presented in Appendix 4.

The method of regression of the standard deviation against the mean concentration for a series of reference samples is conceptually more reliable and generally gives more realistic results. In applying this method to most elements only the replicate analyses of PICG reference samples were used. However, the concentration of some elements in these samples is below detection, in which case data from Bondar Clegg's reference samples were also used. The graphical plots created using this method are presented in Appendix 5.

The detection limits estimated by both methods, together with those quoted by Bondar Clegg, are summarized in Table 2. The practical detection limits recommended for use by the PICG are also presented.

Table 2: Estimated detection limits (ppm)

Element	Bondar Clegg	Method 1	Method 2	Preferred value
Ag	0.2	0.9	1.0	1.0
As	1	4.5	6.1	4.0
Ba	1	2.4	5.4	5.4
Bi	5	-	6.0	6.0
Cd	0.2	1.4	0.7	0.7
Cr	1	4.7	3.7	3.7
Co	1	1.9	2.6	2.6
Cu	1	11.0	4.5	4.5
Fe	0.01%	0.6%	0.3%	0.3%
Hg	0.01	-0.04	0.04	0.04
Li	1	1.0	1.2	1.2
Mn	1	-63.0	34.0	34.0
Mo	1	5.0	1.35	1.35
Ni	1	2.4	3.3	3.3
Pb	2	12.0	4.0	4.0
Sb	0.2	0.74	1.9	1.9
Zn	1	15.0	5.0	5.0

Method 1 is based on an estimation of the standard deviation at zero concentration based on the method of duplicate analyses of Thompson and Howarth (1978). In method 2 the standard deviation at zero concentration is based on the regression of the mean on the standard deviation of replicate analyses of a series of reference samples.

4. CONCLUSIONS AND RECOMMENDATIONS

For future phases of the geochemical survey, it is recommended that the quality of analyses be controlled using the following methods:

i. Regular analyses of stream sediment reference samples and the plotting of analyses on control charts such as those shown in Appendix 2.

The three standards used in the first year of the project (J-1, M-1, and COR-1) do not have suitable concentrations for some of the elements of interest to mineral exploration. Three reference samples (PE-1, M-2 and CN-1) have recently been collected and initial analyses show these are ideal for monitoring almost all of the elements of interest, including Hg, Bi, W, As, Sb, Au, Ag. In the future most emphasis should therefore be placed on the use of these three samples together with J-1.

ii. Between-batch precision should be monitored by duplicate analyses.

As a rapid and approximate check, analytical quality may be assessed by plotting duplicate sets of analyses on scatter plots, as shown in Appendix 3.

For quantitative assessment of precision, duplicate analyses should be plotted in Thompson and Howarth type control charts as shown in Appendix 4. Duplicate analyses from the first year of the project indicate that it would be unrealistic to expect a precision of 10%, which is often taken arbitrarily as an acceptable level for geochemical exploration. For some elements precision is better than 10%, but in general it appears to be in the range 10-20%, and for a few elements it appears to be poorer.

It is recommended that the levels of precision derived empirically from the duplicate analyses of the first year of the project using the method of Thompson and Howarth should at least be maintained during future analytical programmes. The precisions attained for each element are summarized in Table 3 below.

Table 3. Acceptable precision levels

Element	Precision level
Ag	25%
Co	15%
Mn	15%
Sr	25%
As	5%
Cu	20%
Mo	25%
V	20%
Ba	20%
Fe	15%
Ni	10%
Zn	20%
Cd	15%
Hg	15%
Pb	40%
Cr	10%
Li	15%
Sb	10%

5. BIBLIOGRAPHY

DARNLEY A. G., BJÖRKLUND A., BØLVIKEN B., GUSTAVSSON N., KOVAL P. V., PLANT J. A., STEENFELT A., TAUCHID M., XIE XUEJING, GARRETT R. G. and HALL G. E. M. (1995) A global geochemical database for environmental and resource management: Recommendations for international Geochemical Mapping. Final Report of IGCP Project 259. UNESCO, Paris, 122 p.

DUNKLEY P. N., GAIBOR A. and BOLAÑOS J. E. (1997) Geochemical Orientation Survey, Río Junín. Report Number 5. Subcomponent 3.4 Geological Mapping Information Project, 32p.

IUPAC (1978) Nomenclature, symbols units and their usage in spectrochemical analysis. Spectrochim. Acta. B33, 242-246.

THOMPSON M. (1983) Control procedures in geochemical analysis. In: Statistics and data analysis in geochemical prospecting – Handbook of Exploration Geochemistry Vol. 2 (Ed. Howarth R. J.), Elsevier. 39-58.

THOMPSON M. (1988) Variation of precision with concentration in an analytical system. Analyst, 133, 1579-1587.

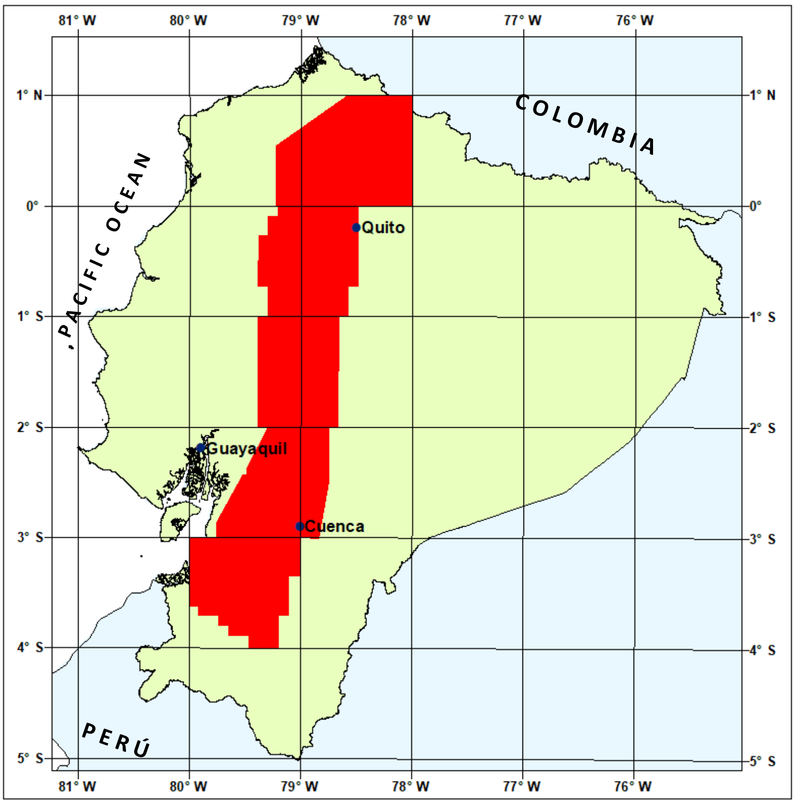
THOMPSON M. and HOWARTH R. J. (1976) Duplicate analyses in geochemical practice (2 parts). Analyst, 101, 690-709.

THOMPSON M. and HOWARTH R. J. (1978) A new approach to the estimation of analytical precision. J. Geochemical Exploration, 9, 23-30.

APPENDIX 1 OF REPORT:

CONTROL OF QUALITY OF GEOCHEMICAL DATA

ANALYTICAL RESULTS



GEOLOGICAL INFORMATION MAPPING PROGRAMME

QUITO, 1997

Analytical results of stream sediment reference samples

Table 1. Reference sample J-1. Original data from laboratory

Au	Ag	Cu	Pb	Zn	Mo	Ni	Co	Cd	Bi	Ba	Cr
-5	0.3	200	7	69	2	9	9	-0.2	-5	67	39
-5	0.5	207	8	74	2	9	9	-0.2	-5	69	41
46	0.3	178	8	74	3	9	10	-0.2	-5	68	40
9	0.6	188	7	70	1	9	9	0.2	-5	71	37
13	0.5	189	7	71	2	9	10	-0.2	-5	68	48
27	0.4	179	7	71	1	9	9	-0.2	-5	68	40
12	0.5	194	7	73	2	8	9	-0.2	-5	71	40
-5	0.5	163	7	77	1	9	9	0.3	-5	63	43
16	0.9	192	7	74	1	9	9	-0.2	-5	62	43
5	0.4	174	7	70	2	9	9	0.2	-5	61	39
35	-0.2	174	4	67	2	8	9	-0.2	-5	62	35
7	-0.2	162	3	67	2	8	9	-0.2	-5	63	39
-5	-0.2	162	2	59	1	10	9	-0.2	-5	62	36
-5	-0.2	175	4	62	-1	10	10	-0.2	-5	64	39
-5	-0.2	161	1	57	1	10	9	-0.2	-5	56	36
-5	0.4	174	2	60	-1	10	9	0.4	-5	60	38
-5	-0.2	182	7	72	2	6	6	-0.2	-5	67	36
6	-0.2	191	7	68	2	6	7	-0.2	-5	63	39
-5	-0.2	191	7	68	3	7	5	-0.2	-5	69	38
-5	-0.2	195	6	71	3	6	6	0.4	-5	67	42
-5	-0.2	166	3	56	1	8	8	-0.2	-5	62	28
-5	-0.2	166	3	61	-1	9	9	-0.2	-5	58	37
-5	-0.2	210	8	73	2	10	11	-0.2	-5	74	45
-5	4.7	187	9	72	2	11	11	-0.2	-5	73	40
6	-0.2	179	-2	66	1	10	10	-0.2	-5	62	41
6	0.3	181	4	68	1	9	9	-0.2	-5	68	39
-5	0.3	168	-2	62	-1	8	9	-0.2	-5	61	36
-5	0.4	192	-2	64	-1	9	9	-0.2	-5	61	41

V	As	Sb	Hg	Fe	Mn	Mg	Ca	Na	K	Sr	Li
149	21.6	3.4	0.096	4.55	381	0.50	0.28	0.03	0.09	20	6
158	16.6	5.2	0.029	4.79	393	0.51	0.29	0.03	0.09	21	6
158	20.3	1.7	0.181	4.78	381	0.49	0.28	0.03	0.09	20	6
145	15.4	1.9	0.051	4.39	392	0.51	0.29	0.03	0.09	21	7
169	14.1	1.4	0.048	5.04	387	0.49	0.30	0.03	0.09	21	6
156	14.3	1.9	0.056	4.72	381	0.50	0.29	0.03	0.09	20	6
160	17.3	2.3	0.065	4.82	384	0.50	0.29	0.03	0.09	21	6
168	12.4	2.9	0.049	5.08	389	0.49	0.30	0.02	0.08	19	6
167	22	1.8	0.084	5.12	397	0.50	0.30	0.03	0.08	19	6
153	15.7	2.5	0.082	4.64	381	0.47	0.28	0.02	0.08	18	6
139	11.1	1.4	0.055	4.08	368	0.47	0.29	0.02	0.08	20	5
153	13.2	2.2	0.112	4.36	361	0.44	0.28	0.02	0.08	20	5
145	12.2	1.6	0.093	4.61	368	0.48	0.29	0.02	0.08	19	5
158	14	2	0.071	5.03	388	0.51	0.30	0.02	0.08	20	6
146	14.1	2	0.103	4.29	368	0.44	0.27	0.02	0.08	18	5
153	16.4	4.2	0.074	4.85	387	0.45	0.29	0.02	0.08	20	5
154	11	1.9	0.047	4.59	371	0.53	0.33	0.02	0.08	23	7
166	18	2.8	0.051	4.92	376	0.52	0.33	0.02	0.08	23	7
159	12.7	2.6	0.158	4.84	436	0.52	0.33	0.03	0.10	22	6
169	11.2	2.5	0.102	5.14	437	0.51	0.32	0.03	0.09	21	6
118	19.3	4.2	0.085	3.47	356	0.44	0.25	0.02	0.08	19	5
152	16.4	1.8	0.062	4.43	375	0.46	0.30	0.02	0.08	20	5
190	12.6	3.4	0.088	5.14	417	0.50	0.32	0.03	0.10	23	7
169	13.5	2.9	0.094	4.59	408	0.49	0.31	0.03	0.10	23	7
160	14.5	2.4	0.054	4.88	425	0.51	0.33	0.03	0.09	22	5
162	16.2	1.5	0.049	4.73	432	0.51	0.34	0.03	0.09	23	6
150	11	3.1	0.218	4.42	396	0.49	0.30	0.02	0.08	21	6
164	10.7	6.6	0.194	4.78	416	0.49	0.32	0.03	0.08	21	6

Table 2. Reference sample M-1. Original data from laboratory

Au	**Ag**	**Cu**	**Pb**	**Zn**	**Mo**	**Ni**	**Co**	**Cd**	**Bi**	**Ba**	**Cr**
-5	0.5	87	8	67	1	14	12	-0.2	-5	60	60
6	0.2	89	13	64	1	14	12	-0.2	-5	61	57
7	0.5	81	16	61	1	12	11	-0.2	-5	53	50
-5	0.4	88	11	63	2	13	12	-0.2	-5	60	54
-5	0.5	85	7	66	-1	13	11	-0.2	-5	57	56
9	0.4	82	8	66	-1	13	12	-0.2	-5	64	56
6	0.6	76	10	66	-1	13	11	-0.2	-5	53	53
10	0.8	83	10	66	-1	13	11	-0.2	-5	53	57
52	0.6	79	7	65	-1	12	11	-0.2	-5	52	52
9	0.5	82	11	64	-1	13	11	-0.2	-5	51	55
-5	-0.2	80	4	61	2	13	11	-0.2	-5	51	52
-5	-0.2	77	11	63	2	13	11	-0.2	-5	54	50
-5	0.4	76	2	58	-1	15	12	-0.2	-5	55	58
-5	0.3	76	5	57	6	16	12	-0.2	6	53	81
-5	0.2	85	-2	58	-1	14	12	-0.2	9	50	63
-5	-0.2	91	3	51	2	13	11	-0.2	7	48	53
-5	-0.2	89	7	66	4	10	7	-0.2	7	60	56
27	-0.2	88	9	66	4	11	7	-0.2	10	57	56
-5	-0.2	86	9	70	4	8	7	0.4	-5	63	58
7	0.2	83	9	63	3	10	6	0.5	6	57	56
-5	0.2	69	2	53	3	18	11	-0.2	6	46	61
-5	0.3	78	2	51	1	13	10	-0.2	-5	48	50
-5	-0.2	79	7	57	1	13	12	-0.2	-5	62	55
-5	-0.2	89	8	56	1	13	11	-0.2	-5	64	50
-5	0.2	75	-2	57	-1	13	11	-0.2	-5	51	56
-5	-0.2	78	-2	57	-1	12	11	-0.2	-5	52	55
-5	0.3	85	-2	55	-1	13	11	-0.2	6	55	53
-5	0.4	92	3	57	-1	13	11	-0.2	-5	49	58

V	**As**	**Sb**	**Hg**	**Fe**	**Mn**	**Mg**	**Ca**	**Na**	**K**	**Sr**	**Li**
253	11.5	1	0.04	6.99	362	0.41	0.35	0.05	0.08	30	6
245	8.2	0.7	0.047	6.81	360	0.41	0.34	0.05	0.07	30	6
218	12.4	2.4	0.043	6.13	333	0.37	0.32	0.04	0.07	27	6
229	7.8	1.1	0.019	6.34	349	0.4	0.34	0.05	0.07	30	6
234	8.5	0.9	0.027	6.52	355	0.41	0.34	0.05	0.08	30	6
244	8.9	1	0.039	6.77	362	0.4	0.34	0.05	0.07	30	6
223	10.5	0.9	0.043	6.34	352	0.41	0.35	0.04	0.07	28	6
237	9.4	0.7	0.038	6.73	357	0.4	0.35	0.04	0.07	27	6
220	8.1	1.2	0.036	6.2	339	0.37	0.33	0.04	0.07	27	5
240	9	1.8	0.038	6.64	345	0.36	0.32	0.04	0.06	26	5
218	7.8	1.2	0.037	6.44	341	0.38	0.34	0.04	0.07	26	5
216	7.5	0.6	0.074	5.81	336	0.36	0.32	0.03	0.07	25	5
263	7.9	2.6	0.038	7.88	358	0.4	0.34	0.04	0.06	29	5
285	9.4	0.7	0.054	8.47	362	0.4	0.34	0.04	0.06	29	5
272	9	1.3	0.035	7.38	385	0.39	0.35	0.04	0.07	29	5
230	9.3	1.9	0.054	6.26	349	0.37	0.33	0.04	0.07	28	5
257	14.7	1.5	0.03	6.94	344	0.44	0.4	0.05	0.06	36	7
258	12.1	1.4	0.053	6.86	351	0.43	0.41	0.05	0.07	37	7
265	6.4	0.9	0.03	7.32	422	0.47	0.42	0.06	0.09	36	7
232	8.6	2.4	0.078	6.5	374	0.42	0.36	0.05	0.08	30	6
235	10.6	1.2	0.015	6.37	336	0.35	0.31	0.04	0.06	26	5
203	9.7	-0.2	0.03	5.57	315	0.35	0.31	0.04	0.06	26	5
253	7.7	1.2	0.025	6.45	359	0.4	0.35	0.05	0.08	31	7
223	8.3	0.5	0.055	5.54	344	0.4	0.33	0.05	0.08	31	7
230	9.1	1	0.026	6.44	372	0.4	0.38	0.05	0.07	33	5
234	6.9	0.9	0.02	6.62	381	0.4	0.38	0.05	0.07	34	5
236	8.2	1.4	0.016	6.45	359	0.38	0.35	0.04	0.07	31	5
256	6.7	1.5	0.034	6.88	361	0.37	0.36	0.05	0.07	32	5

Table 3. Reference sample COR-1. Original data from laboratory

Au	Ag	Cu	Pb	Zn	Mo	Ni	Co	Cd	Bi	Ba	Cr
16	0.4	22	13	58	-1	15	12	-0.2	-5	51	61
-5	0.4	29	10	59	-1	16	12	-0.2	-5	50	61
-5	0.3	21	33	62	-1	16	12	-0.2	-5	50	67
-5	0.2	22	8	66	-1	17	13	-0.2	-5	56	71
-5	8.1	20	6	56	-1	15	12	-0.2	-5	52	60
9	0.3	21	11	63	-1	16	13	-0.2	-5	53	66
13	0.4	21	10	60	-1	14	12	-0.2	-5	49	64
9	0.3	22	8	58	-1	15	12	-0.2	-5	52	61
7	0.6	19	8	61	-1	15	12	-0.2	-5	52	63
-5	0.5	19	8	60	-1	15	11	-0.2	-5	49	62
-5	-0.2	19	8	56	-1	15	12	-0.2	-5	47	60
-5	-0.2	19	4	61	2	16	12	-0.2	-5	46	66
-5	0.5	20	4	50	-1	18	12	-0.2	-5	47	60
-5	0.4	20	17	54	-1	17	12	-0.2	-5	47	62
-5	0.3	20	-2	47	-1	15	12	-0.2	-5	41	61
-5	0.3	22	2	51	-1	17	12	-0.2	6	46	66
32	-0.2	15	19	60	2	12	8	-0.2	-5	50	62
-5	-0.2	12	6	49	3	10	7	-0.2	6	49	54
13	-0.2	16	9	59	2	11	6	-0.2	-5	54	61
5	-0.2	29	9	57	4	12	7	-0.2	-5	54	60
-5	0.3	24	-2	48	-1	15	11	-0.2	-5	44	56
-5	-0.2	22	5	51	-1	16	11	-0.2	-5	43	57
-5	-0.2	15	12	61	-1	16	15	-0.2	-5	56	69
-5	-0.2	27	13	51	-1	16	13	1	-5	53	61
10	0.3	21	2	53	-1	17	12	-0.2	-5	45	67
-5	0.2	22	-2	55	-1	17	13	-0.2	-5	43	74
-5	0.4	20	-2	48	-1	14	11	-0.2	-5	44	56
-5	0.4	21	-2	52	-1	16	12	-0.2	-5	47	61
V	**As**	**Sb**	**Hg**	**Fe**	**Mn**	**Mg**	**Ca**	**Na**	**K**	**Sr**	**Li**
268	5.5	-0.2	0.03	7.27	329	0.35	0.37	0.06	0.06	35	6
279	5.9	0.3	0.023	7.6	335	0.34	0.37	0.06	0.06	35	6
306	5.4	0.4	0.023	8.11	347	0.34	0.36	0.06	0.06	34	6
317	7	0.3	0.014	8.43	355	0.36	0.38	0.06	0.06	36	6
264	5.5	0.4	0.01	7.7	316	0.33	0.35	0.06	0.06	33	6
297	5.9	0.3	0.09	7.88	336	0.35	0.37	0.06	0.06	38	6
291	5.5	0.4	0.011	7.69	333	0.33	0.36	0.06	0.06	35	6
277	5	1.4	0.018	7.34	330	0.34	0.36	0.06	0.06	35	6
281	6.3	0.4	0.021	7.55	325	0.33	0.35	0.05	0.06	32	5
269	5.1	0.6	0.01	7.21	310	0.31	0.33	0.05	0.05	30	5
265	5.3	-0.2	0.037	7.59	333	0.34	0.38	0.05	0.06	32	5
282	5.4	0.2	0.023	7.23	334	0.32	0.35	0.04	0.06	31	5
277	5.3	0.3	0.032	8.12	329	0.35	0.36	0.05	0.05	33	5
292	4.9	1	0.027	8.52	329	0.36	0.36	0.05	0.06	34	5
272	4.8	0.5	0.018	7.3	324	0.32	0.35	0.05	0.06	32	4
295	5.3	0.6	0.026	7.72	341	0.32	0.37	0.05	0.06	36	5
285	5.5	0.6	0.018	7.6	340	0.4	0.45	0.06	0.06	45	7
253	4.2	0.4	0.01	6.56	279	0.29	0.37	0.05	0.05	36	6
282	4.1	0.4	0.015	7.46	347	0.33	0.4	0.07	0.07	37	6
274	1.2	0.4	0.015	7.26	351	0.35	0.4	0.07	0.06	39	6
262	6.4	0.5	0.028	6.93	313	0.31	0.35	0.05	0.05	33	5
264	6.5	-0.2	0.017	6.88	323	0.33	0.36	0.05	0.06	34	5
328	4.8	0.3	0.015	7.87	343	0.34	0.37	0.06	0.07	37	6
290	4.7	0.3	0.06	6.86	312	0.31	0.32	0.05	0.06	32	6
293	5	0.5	0.016	7.94	364	0.34	0.42	0.06	0.06	40	5
330	5.4	0.4	0.017	8.83	372	0.34	0.41	0.06	0.06	39	5
255	4	0.5	0.05	6.83	329	0.33	0.39	0.06	0.06	39	5
282	4.3	0.5	0.053	7.44	347	0.34	0.4	0.06	0.06	40	5

Table 4. Reference sample J-1. Values below detection set to 2/3 detection limit prior to calculation of the mean, standard deviation and coefficient of variation.

J-1	Ag	Cu	Pb	Zn	Mo	Ni	Co	Fe	Mn	Ba	Cr	V	Sr	Li	As	Sb	Hg
	0.3	200	7	69	2	9	9	4.55	381	67	39	149	20	6	21.6	3.4	0.096
	0.5	207	8	74	2	9	9	4.79	393	69	41	158	21	6	16.6	5.2	0.029
	0.3	178	8	74	3	9	10	4.78	381	68	40	158	20	6	20.3	1.7	0.181
	0.6	188	7	70	1	9	9	4.39	392	71	37	145	21	7	15.4	1.9	0.051
	0.5	189	7	71	2	9	10	5.04	387	68	48	169	21	6	14.1	1.4	0.048
	0.4	179	7	71	1	9	9	4.72	381	68	40	156	20	6	14.3	1.9	0.056
	0.5	194	7	73	2	8	9	4.82	384	71	40	160	21	6	17.3	2.3	0.065
	0.5	163	7	77	1	9	9	5.08	389	63	43	168	19	6	12.4	2.9	0.049
	0.9	192	7	74	1	9	9	5.12	397	62	43	167	19	6	22	1.8	0.084
	0.4	174	7	70	2	9	9	4.64	371	61	39	153	18	6	15.7	2.5	0.082
	0.133	174	4	67	2	8	9	4.08	368	62	35	139	20	5	11.1	1.4	0.055
	0.133	162	3	67	2	8	9	4.36	361	63	39	153	20	5	13.2	2.2	0.112
	0.133	162	2	59	1	10	9	4.61	368	62	36	145	19	5	12.2	1.6	0.093
	0.133	175	4	62	0.66	10	10	5.03	388	64	39	158	20	6	14	2	0.071
	0.133	161	1	57	1	10	9	4.29	368	56	36	146	18	5	14.1	2	0.103
	0.4	174	2	60	0.66	10	9	4.85	387	60	38	153	20	5	16.4	4.2	0.074
	0.133	182	7	72	2	6	6	4.59	371	67	36	154	23	7	11	1.9	0.047
	0.133	191	7	68	2	6	7	4.92	376	63	39	166	23	7	18	2.8	0.051
	0.133	191	7	68	3	7	5	4.84	436	69	38	159	22	6	12.7	2.6	0.158
	0.133	195	6	71	3	6	6	5.14	437	67	42	169	21	6	11.2	2.5	0.102
	0.133	166	3	56	1	8	8	3.47	356	62	28	118	19	5	19.3	4.2	0.085
	0.133	166	3	61	0.66	9	9	4.43	375	58	37	152	20	5	16.4	1.8	0.062
	0.133	210	8	73	2	10	11	5.14	417	74	45	190	23	7	12.6	3.4	0.088
		187	9	72	2	11	11	4.59	408	73	40	169	23	7	13.5	2.9	0.094
	0.133	179	1.33	66	1	10	10	4.88	425	62	41	160	22	5	14.5	2.4	0.054
	0.3	181	4	68	1	9	9	4.73	432	68	39	162	23	6	16.2	1.5	0.049
	0.3	168	1.33	62	0.66	8	9	4.42	396	61	36	150	21	6	11	3.1	0.218
	0.4	192	1.33	64	0.66	9	9	4.78	416	61	41	164	21	6	10.7	6.6	0.194
Mean	0.30	181.43	5.21	67.71	1.55	8.71	8.82	4.68	390.75	65.00	39.11	156.79	20.64	5.89	14.92	2.65	0.09
SD	0.20	13.74	2.55	5.64	0.75	1.27	1.36	0.36	22.79	4.55	3.63	12.72	1.50	0.69	3.20	1.21	0.05
CV	66.36	7.57	48.99	8.32	48.55	14.60	15.44	7.77	5.83	6.99	9.29	8.11	7.25	11.63	21.45	45.56	54.02

Table 5. Reference sample M-1. Values below detection set to 2/3 detection limit prior to calculation of the mean, standard deviation and coefficient of variation.

M-1	Ag	Cu	Pb	Zn	Ni	Co	Fe	Mn	Ba	Cr	V	Sr	Li	As	Sb	Hg
	0.5	87	8	67	14	12	6.99	362	60	60	253	30	6	11.5	1	0.04
	0.2	89	13	64	14	12	6.81	360	61	57	245	30	6	8.2	0.7	0.047
	0.5	81	16	61	12	11	6.13	333	53	50	218	27	6	12.4	2.4	0.043
	0.4	88	11	63	13	12	6.34	349	60	54	229	30	6	7.8	1.1	0.019
	0.5	85	7	66	13	11	6.52	355	57	56	234	30	6	8.5	0.9	0.027
	0.4	82	8	66	13	12	6.77	362	64	56	244	30	6	8.9	1	0.039
	0.6	76	10	66	13	11	6.34	352	53	53	223	28	6	10.5	0.9	0.043
	0.8	83	10	66	13	11	6.73	357	53	57	237	27	6	9.4	0.7	0.038
	0.6	79	7	65	12	11	6.2	339	52	52	220	27	5	8.1	1.2	0.036
	0.5	82	11	64	13	11	6.64	345	51	55	240	26	5	9	1.8	0.038
	0.133	80	4	61	13	11	6.44	341	51	52	218	26	5	7.8	1.2	0.037
	0.133	77	11	63	13	11	5.81	336	54	50	216	25	5	7.5	0.6	0.074
	0.4	76	2	58	15	12	7.88	358	55	58	263	29	5	7.9	2.6	0.038
	0.3	76	5	57	16	12	8.47	362	53	81	285	29	5	9.4	0.7	0.054
	0.2	85	1.33	58	14	12	7.38	385	50	63	272	29	5	9	1.3	0.035
	0.133	91	3	51	13	11	6.26	349	48	53	230	28	5	9.3	1.9	0.054
	0.133	89	7	66	10	7	6.94	344	60	56	257	36	7	14.7	1.5	0.03
	0.133	88	9	66	11	7	6.86	351	57	56	258	37	7	12.1	1.4	0.053
	0.133	86	9	70	8	7	7.32	422	63	58	265	36	7	6.4	0.9	0.03
	0.133	83	9	63	10	6	6.5	374	57	52	232	30	6	8.6	2.4	0.078
	0.2	69	2	53	18	11	6.37	336	46	61	235	26	5	10.6	1.2	0.015
	0.3	78	2	51	13	10	5.57	315	48	50	203	26	5	9.7	0.133	0.03
	0.133	79	7	57	13	12	6.45	359	62	55	253	31	7	7.7	1.2	0.025
	0.133	89	8	56	13	11	5.54	344	64	50	223	31	7	8.3	0.5	0.055
	0.2	75	1.33	57	13	11	6.44	372	51	56	230	33	5	9.1	1	0.026
	0.133	78	1.33	57	12	11	6.62	381	52	55	234	34	5	6.9	0.9	0.02
	0.3	85	1.33	55	13	11	6.45	359	55	53	236	31	5	8.2	1.4	0.016
	0.4	92	3	57	13	11	6.88	361	49	58	256	32	5	6.7	1.5	0.034
Mean	0.31	82.43	6.69	60.86	12.89	10.64	6.63	355.82	54.96	55.96	239.61	29.79	5.68	9.08	1.22	0.038
SD	0.19	5.68	4.05	5.22	1.83	1.70	0.62	19.86	5.17	5.95	19.09	3.21	0.77	1.86	0.58	0.015
REL DEV	60.76	6.89	60.61	8.58	14.21	16.01	9.34	5.58	9.40	10.63	7.97	10.79	13.60	20.44	47.98	40.165

Table 6. Reference sample COR-1. Values below detection set to 2/3 detection limit prior to calculation of the mean, standard deviation and coefficient of variation.

COR-1	Ag	Cu	Pb	Zn	Ni	Co	Fe	Mn	Ba	Cr	V	Sr	Li	As	Sb	Hg
	0.4	22	13	58	15	12	7.27	329	51	61	268	35	6	5.5	0.133	0.03
	0.4	29	10	59	16	12	7.6	335	50	61	279	35	6	5.9	0.3	0.023
	0.3	21	33	62	16	12	8.11	347	50	67	306	34	6	5.4	0.4	0.023
	0.2	22	8	66	17	13	8.43	355	56	71	317	36	6	7	0.3	0.014
		20	6	56	15	12	7.07	316	52	60	264	33	6	5.5	0.4	0.01
	0.3	21	11	63	16	13	7.88	336	53	66	297	36	6	5.9	0.3	0.09
	0.4	21	10	60	14	12	7.69	333	49	64	291	35	6	5.5	0.4	0.011
	0.3	22	8	58	15	12	7.34	330	52	61	277	35	6	5	1.4	0.018
	0.6	19	8	61	15	12	7.55	325	52	63	281	32	5	6.3	0.4	0.021
	0.5	19	8	60	15	11	7.21	310	49	62	269	30	5	5.1	0.6	0.01
	0.133	19	8	56	15	12	7.59	333	47	60	265	32	5	5.3	0.133	0.037
	0.133	19	4	61	16	12	7.23	334	46	66	282	31	5	5.4	0.2	0.023
	0.5	20	4	50	18	12	8.12	329	47	60	277	33	5	5.3	0.3	0.032
	0.4	20	17	54	17	12	8.52	329	47	62	292	34	5	4.9	1	0.027
	0.3	20	1.33	47	15	12	7.3	324	41	61	272	32	4	4.8	0.5	0.018
	0.3	22	2	51	17	12	7.72	341	46	66	295	36	5	5.3	0.6	0.026
	0.133	15	19	60	12	8	7.6	340	50	62	285	45	7	5.5	0.6	0.018
	0.133	12	6	49	10	7	6.56	279	49	54	253	36	6	4.2	0.4	0.01
	0.133	16	9	59	11	6	7.46	347	54	61	282	37	6	4.1	0.4	0.015
	0.133	29	9	57	12	7	7.26	351	54	60	274	39	6	1.2	0.4	0.015
	0.3	24	1.33	48	15	11	6.93	313	44	56	262	33	5	6.4	0.5	0.028
	0.133	22	5	51	16	11	6.88	323	43	57	264	34	5	6.5	0.133	0.017
	0.133	15	12	61	16	15	7.87	343	56	69	328	37	6	4.8	0.3	0.015
	0.133	27	13	51	16	13	6.86	312	53	61	290	32	6	4.7	0.3	0.06
	0.3	21	2	53	17	12	7.94	364	45	67	293	40	5	5	0.5	0.016
	0.2	22	1.33	55	17	13	8.83	372	43	74	330	39	5	5.4	0.4	0.017
	0.4	20	1.33	48	14	11	6.83	329	44	56	255	39	5	4	0.5	0.05
	0.4	21	1.33	52	16	12	7.44	347	47	61	282	40	5	4.3	0.5	0.053
Mean	0.29	20.71	8.27	55.93	15.14	11.39	7.54	333.07	48.93	62.46	283.21	35.36	5.50	5.15	0.44	0.026
SD	0.14	3.73	6.81	5.21	1.90	2.01	0.54	18.26	4.08	4.53	19.67	3.32	0.64	1.06	0.26	0.018
REL DEV	48.40	18.01	82.35	9.32	12.54	17.61	7.20	5.48	8.34	7.26	6.94	9.40	11.61	20.54	58.79	69.298

Table 7. Bondar Clegg Au reference samples

Batch	**High Gold Standard Au (ppb)**	**Low Gold Standard Au (ppb)**
3	705	24
4	747	21
4	735	20
5	680	26
6	737	23
7	728	21
7	729	23
8	726	21
8	719	24
Mean	722.89	22.56
SD	19.92	1.94
CV	2.76	8.62

Table 8. BGS Geochemical STD-3 (Bondar Clegg reference sample)

STD-3	**Ag**	**Cu**	**Pb**	**Zn**	**Mo**	**Ni**	**Co**	**Cd**	**Bi**	**Fe**	**Mn**	**Ba**	**Cr**	**V**	**As**	**Sb**	**Hg**
	6.6	788	210	452	520	560	36	2.4	7	4.18	774	182	144	31	293.3		
	6.3	836	211	448	529	506	37	2.5	9	4.39	805	202	142	32	326.4	43.1	3.652
	7.6	903	230	499	550	574	44	3.4	3.33	4.42	818	241	153	33	359.8	40	3.693
	7.4	859	219	476	527	552	42	3.9	3.33	4.22	779	231	145	31	332.4	40.2	3.469
	7.4	853	210	486	503	485	34	3.6	10	4.22	876	230	144	31	331	31	3.669
	7	801	216	447	503	485	36	2.5	9	3.83	774	198	131	30	328.4	40.8	3.827
	6.4	935	207	501	515	489	38	2.1	15	4	825	238	137	32	315.4	46.2	3.222
	7.8	825	204	468	483	465	37	2.7	5	4.14	816	206	148	33	309.6	47.1	3.427
	6.4	870	214	484	518	497	37	2.6	7	4.11	833	213	146	35	292.2	45.1	3.145
	7.5	855	198	454	477	466	36	2.2	6	3.84	798	189	134	32	298.3	52.7	3.407
Mean	7.04	852.50	211.90	471.50	512.50	507.90	37.70	2.79	7.47	4.14	809.80	213.00	142.40	32.00	318.68	42.91	3.50
SD	0.57	44.16	8.74	20.72	21.84	39.66	3.02	0.62	3.51	0.20	31.50	20.96	6.65	1.41	21.18	6.03	0.23
CV	3.80	294.41	58.24	138.14	145.59	264.37	20.14	4.13	23.39	1.34	210.02	139.74	44.35	9.43	141.23	40.22	1.52

Table 9. BGS Geochemical STD-4 (Bondar Clegg reference sample)

STD-4	Ag	Cu	Pb	Zn	Mo	Ni	Co	Fe	Mn	Ba	Cr	V	As	Sb	Hg
	1	264	32	224	3	43	9	2.42	571	58	72	8	32.6	0.3	0.038
	0.8	270	32	227	3	43	9	2.42	577	59	72	9	31.5	0.4	0.026
	1.1	265	33	219	3	39	9	2.28	577	52	72	8	29.1	0.6	0.035
	0.9	281	30	229	2	47	10	2.54	599	56	75	9	31.5	0.5	0.037
	0.6	321	37	248	5	47	10	2.56	590	68	85	9	32.9	0.9	0.041
	1	299	35	239	4	39	7	2.42	634	66	80	8	27.1	0.5	0.033
	0.8	268	35	223	4	44	8	2.25	568	51	77	8	33.6	0.5	0.035
	0.4	317	34	258	4	45	10	2.38	612	68	78	8	30	0.5	0.04
	0.8	304	33	259	3	46	9	2.57	648	67	86	9	29.5	0.3	0.028
	0.8	276	30	227	2	40	9	2.29	593	54	75	8	29.6	0.6	0.017
Mean	0.82	286.50	33.10	235.30	3.30	43.30	9.00	2.41	596.90	59.90	77.20	8.40	30.74	0.51	0.03
SD	0.20	21.87	2.23	14.81	0.95	3.09	0.94	0.12	27.04	6.79	5.14	0.52	2.02	0.17	0.01
CV	24.93	7.64	6.75	6.29	28.75	7.14	10.48	4.84	4.53	11.34	6.66	6.15	6.58	33.90	22.41

Table 10. BGS Geochemical STD-5 (Bondar Clegg reference sample)

STD-5	Ag	Cu	Pb	Zn	Ni	Co	Fe	Mn	Ba	Cr	V	As	Sb	Hg
	0.8	89	11	69	35	16	4.19	702	188	45	110	7.8		
	0.7	91	10	65	32	15	3.81	691	167	45	108	8.3	0.7	0.046
	0.133	103	15	82	39	16	4.33	731	210	54	126	7.9	0.7	0.034
	0.7	93	11	75	32	12	4.03	760	202	46	113	6.1	0.4	0.037
	0.6	97	9	78	31	13	4.22	788	208	48	116	7	0.6	0.04
	0.9	93	12	70	35	16	3.81	704	171	48	108	9.5	1	0.044
	0.7	92	11	70	35	16	3.83	703	177	45	111	8.9	0.3	0.037
	0.3	104	15	78	36	17	4.13	769	219	50	127	7.4	0.5	0.049
	0.133	103	11	74	35	16	3.9	733	209	47	119	7.2	0.5	0.047
	0.9	85	10	76	33	17	4.27	762	185	49	120	7.9	0.5	0.044
	0.8	86	7	73	33	16	3.99	747	173	46	113	7	0.5	0.042
	1.4	91	9	74	34	16	4.03	756	186	47	118	7.5	0.5	0.035
Mean	0.67	93.92	10.92	73.67	34.17	15.50	4.05	737.17	191.25	47.50	115.75	7.71	0.56	0.04
SD	0.36	6.50	2.31	4.66	2.17	1.51	0.18	31.45	17.70	2.61	6.44	0.91	0.19	0.01
CV	52.96	6.92	21.20	6.32	6.35	9.73	4.55	4.27	9.25	5.50	5.56	11.77	32.98	12.34

Table 11. Interlaboratory comparison of analyses. GIMP reference samples

Analysed by Bondar Clegg (BC) and BGS

Element	J-1		COR-1		M-1	
	BC	BGS	BC	BGS	BC	BGS
Ag	0.3	<0.2	0.3	<0.2	0.3	<0.2
Cu	181.4	175.0	20.7	23.0	82.4	79.5
Pb	5.2	3.5	8.3	5.0	6.7	7.0
Zn	67.7	61.0	55.9	43.0	60.9	50.5
Mo	1.5	1.6	<1	0.5	<1	1.0
Ni	8.7	10.5	15.1	18.5	12.9	14.0
Co	8.8	10.7	11.4	14.8	10.6	12.9
Fe	4.7	4.9	7.5	8.1	6.6	7.0
Mn	390.8	468.0	333.1	375.0	355.8	413.0
Ba	65.0	74.0	48.9	64.5	55.0	73.0
Cr	39.1	44.5	62.5	82.0	56.0	65.0
V	156.8	150.0	283.2	293.5	239.6	226.5
Sr	20.6	28.5	35.4	61.0	29.8	48.0
Li	5.9	5.9	5.5	6.0	5.7	5.5
As	14.9	12.5	5.2	5.0	9.1	7.0
Sb	2.6	3.3	0.4	0.6	1.2	1.4
Hg	0.088	0.050	0.026	<0.01	0.038	<0.01

BGS values are the average of duplicate analyses. Bondar Clegg values are the average of 30 replicate analyses

Table 12. Interlaboratory comparison of analyses BGS reference samples

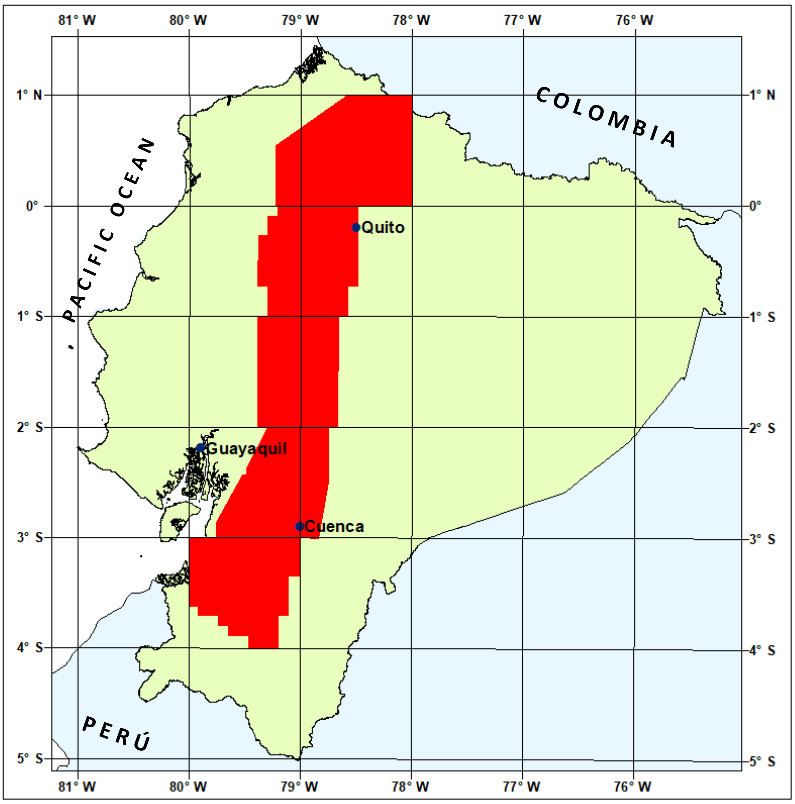
Bondar Clegg (BC) analyses by aqua regia digestion – ICP/AAS. BGS analyses by XRF

Element	S24		S13		S15		S3B	
	BC	BGS	BC	BGS	BC	BGS	BC	BGS
Ag	1.2	4.0					1.3	
Cu	60.5	60.4	16.5	16.1	4.0	4.9	39.0	48.4
Pb	847.5	1114.8	99.0	112.4	17.0	24.7	1464.5	1770.8
Zn	379.0	385.0	114.0	113.8	29.0	28.5	563.5	786.8
Mo	<1	3.7	<1	1.5	<1	1.9	128.0	148.4
Ni	37.5	43.2	24.0	36.5	9.5	11.5	18.5	30.4
Co	70.5	84.6						
Cd	1.4	3.8						
As	122.2	126.0	16.9	15.8	5.2	8.8	3.8	<2
Sb	9.0	6.0						
Ba	504.0	1060.4						

APPENDIX 2 OF REPORT:

CONTROL OF QUALITY OF GEOCHEMICAL DATA

BATCH PRECISION AND ACCURACY CONTROL CHARTS

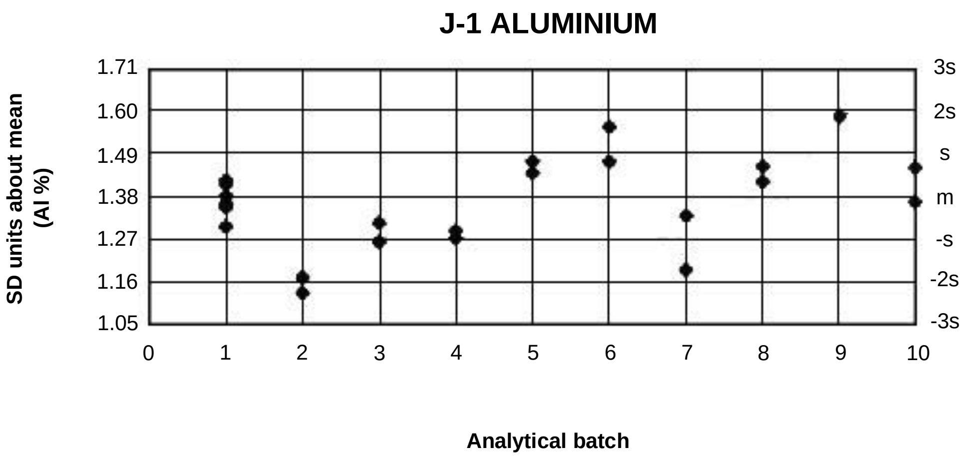


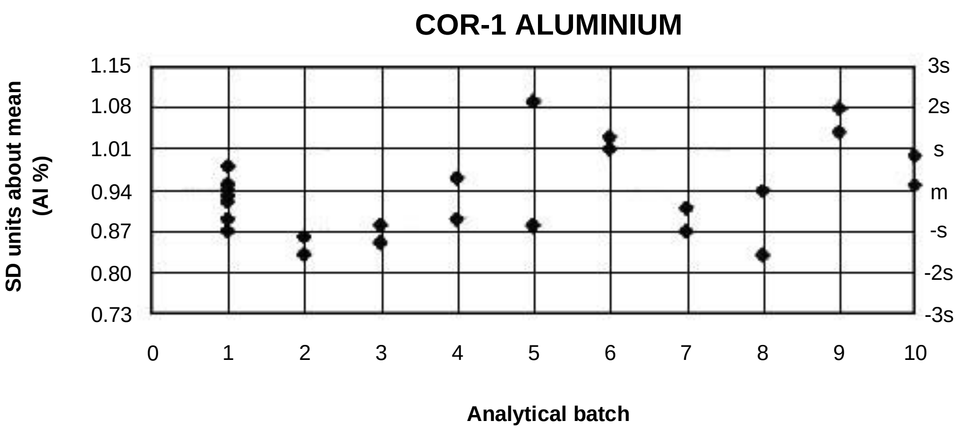
GEOLOGICAL INFORMATION MAPPING PROGRAMME

QUITO, 1997

Control charts showing analyses of reference samples J-1, COR-1, M-1

Analyses from first year. Concentration is plotted against analytical batch, together with mean (m) and standard deviation intervals (s).





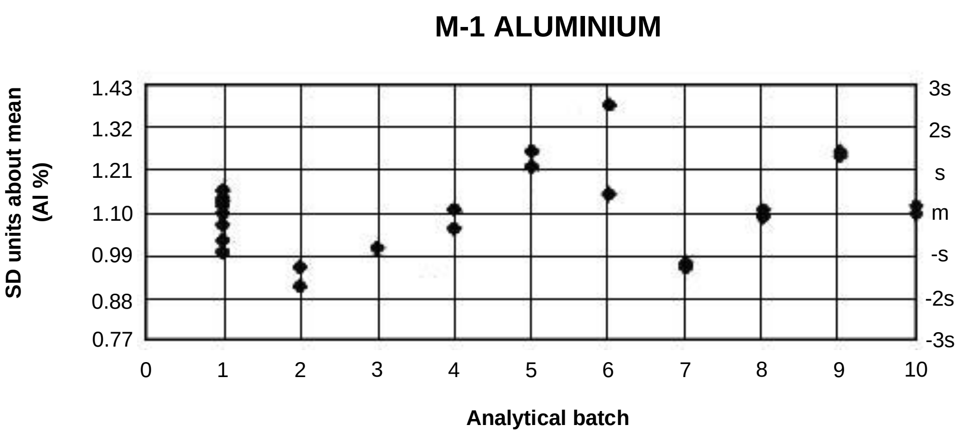
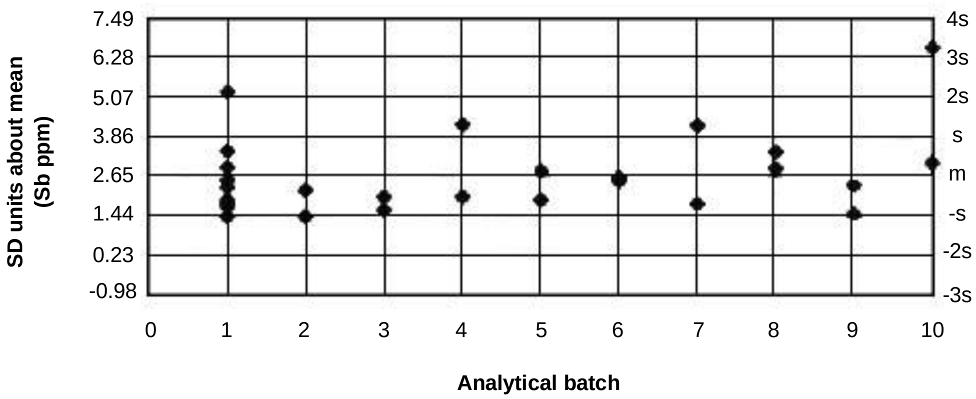
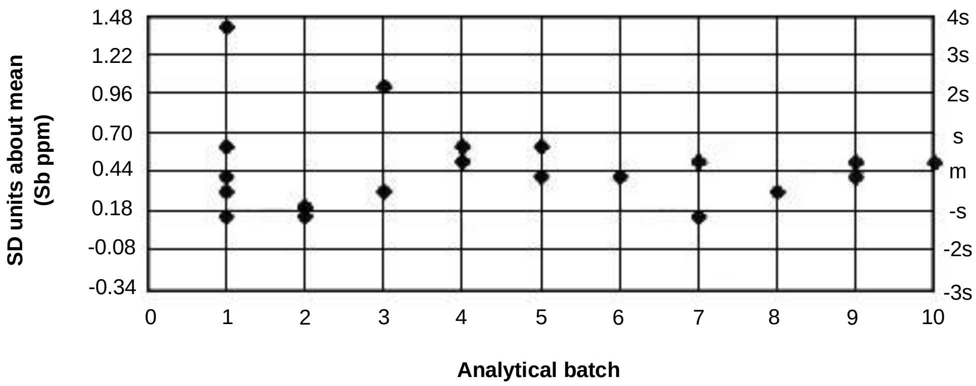


Figure 1. Control charts for Aluminium

J-1 ANTIMONY



COR-1 ANTIMONY



M-1 ANTIMONY

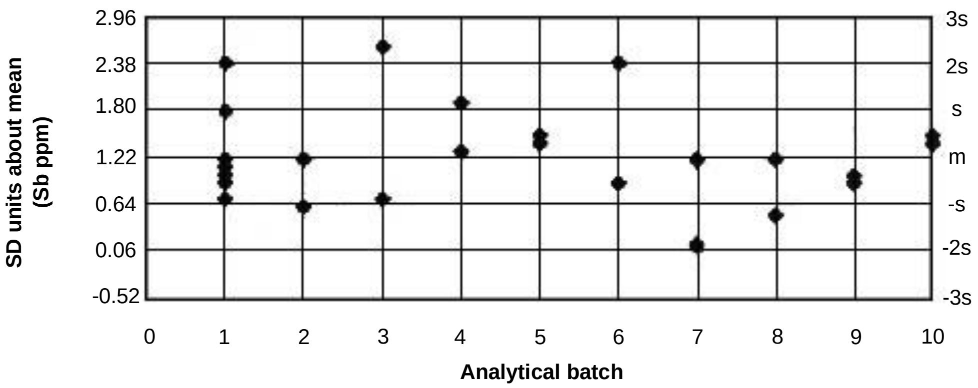
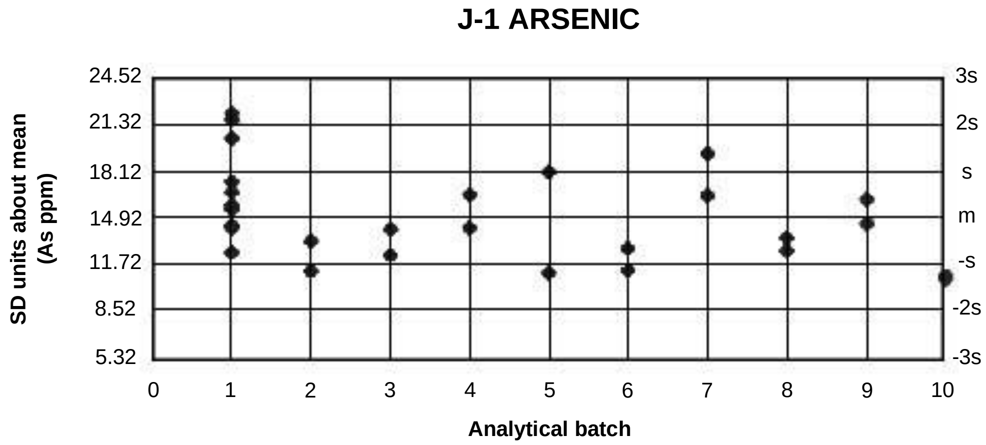
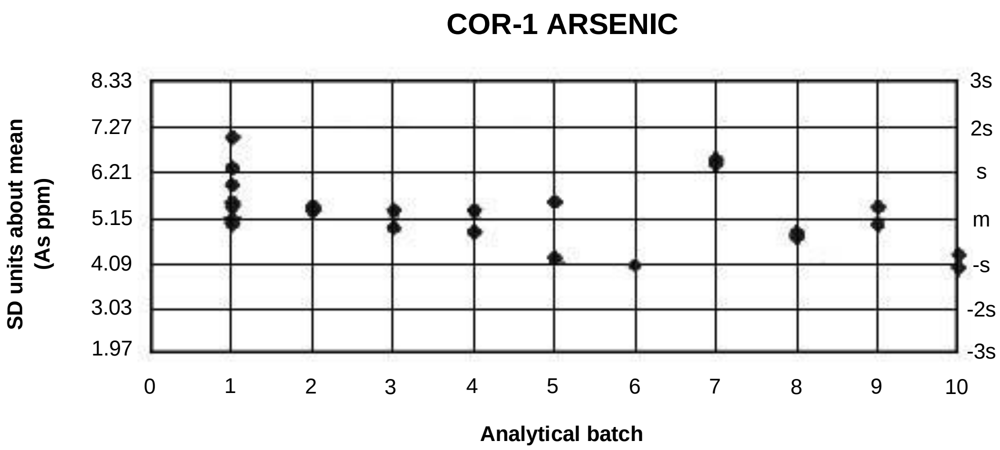


Figure 2. Control charts for Antimony





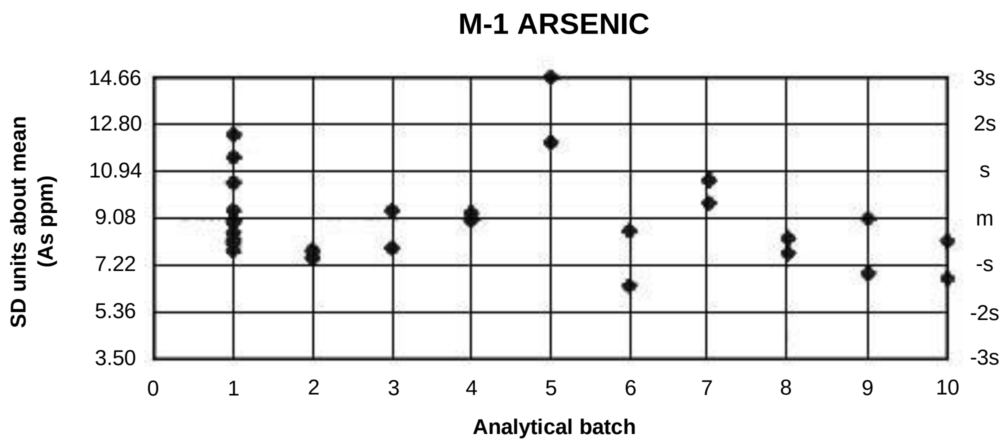
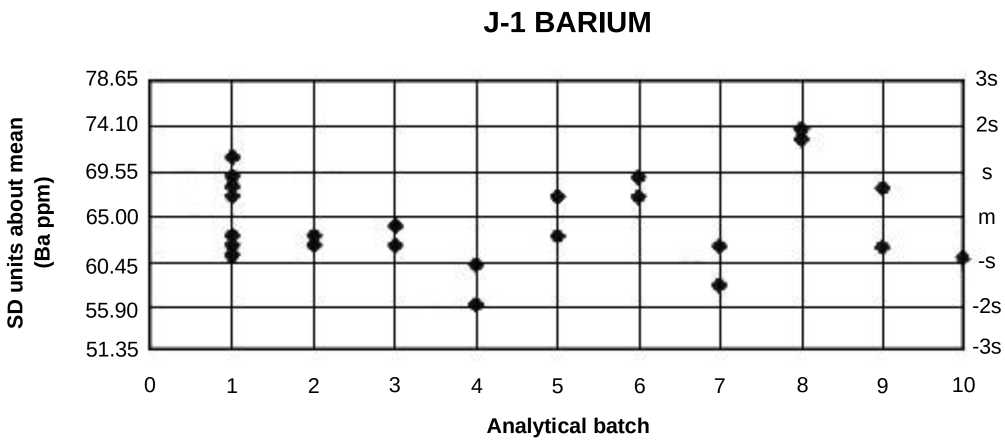
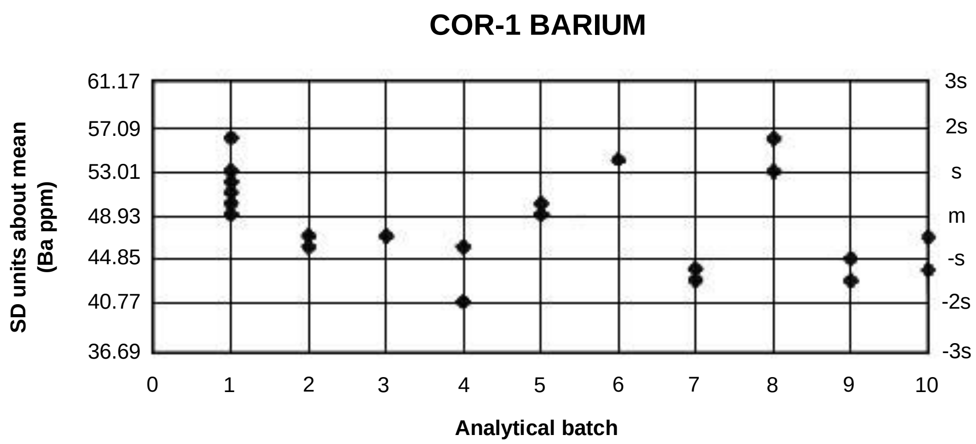


Figure 3. Control charts for Arsenic





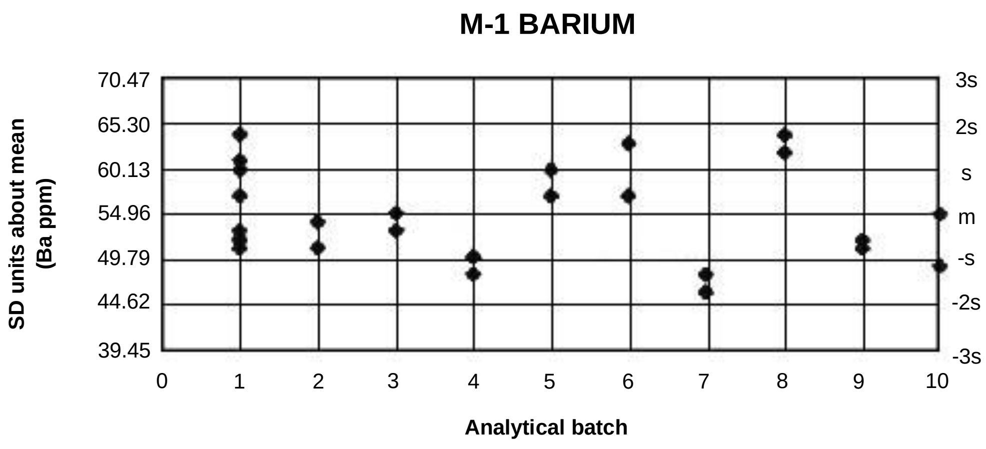
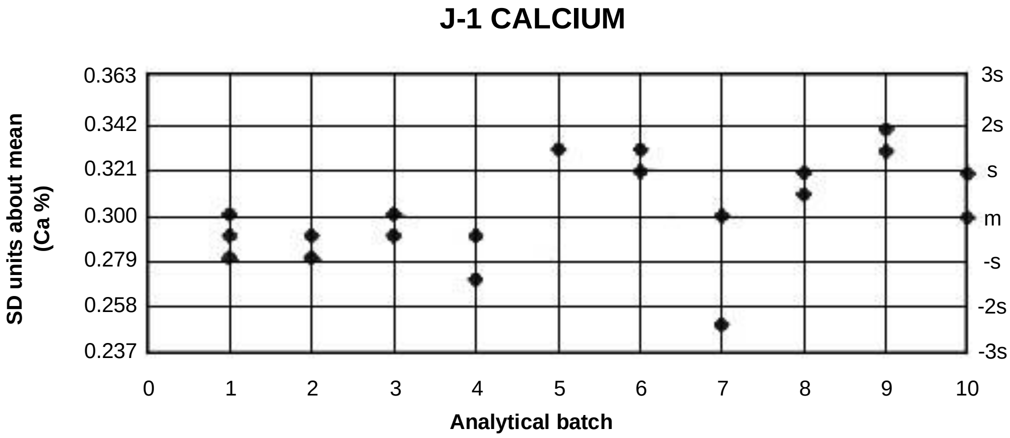
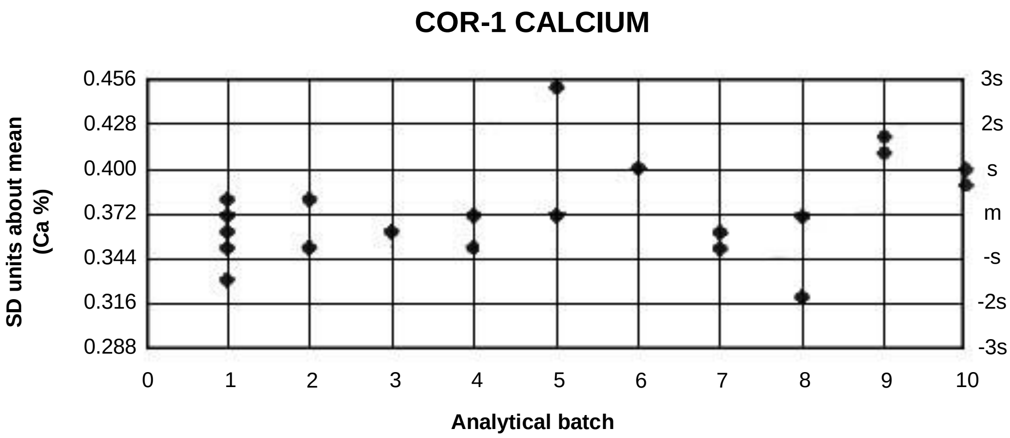


Figure 4. Control charts for Barium





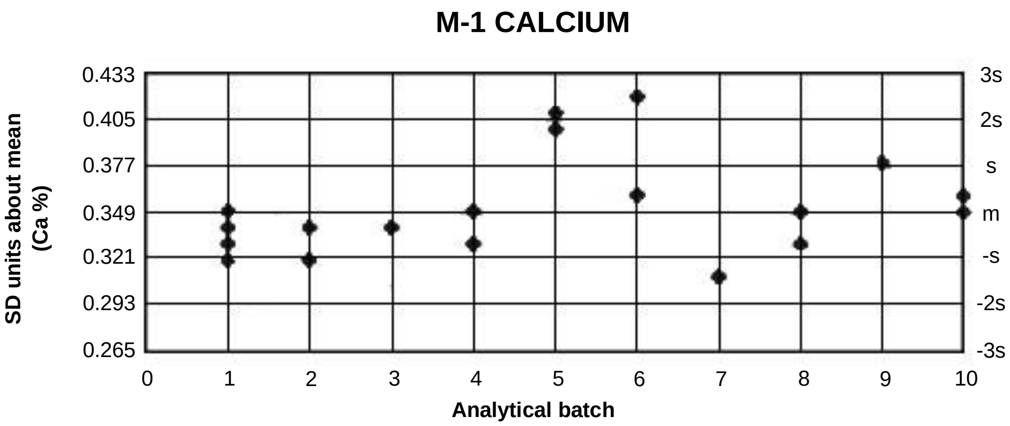
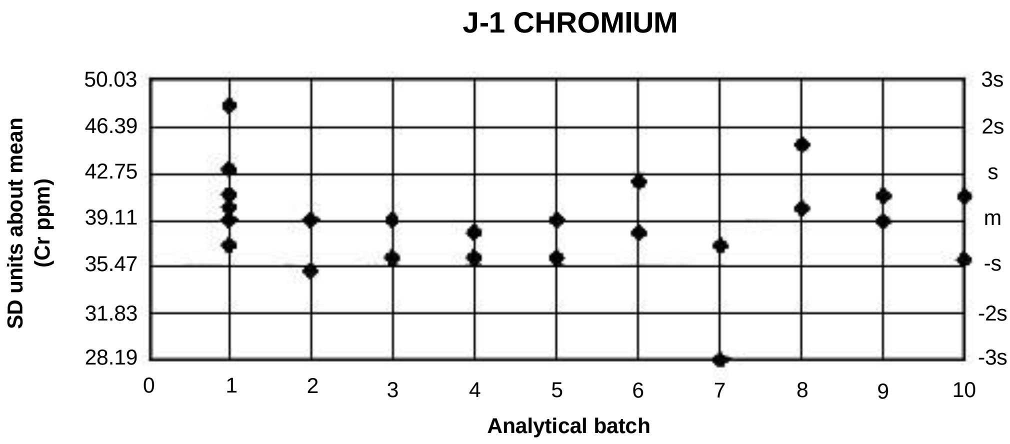
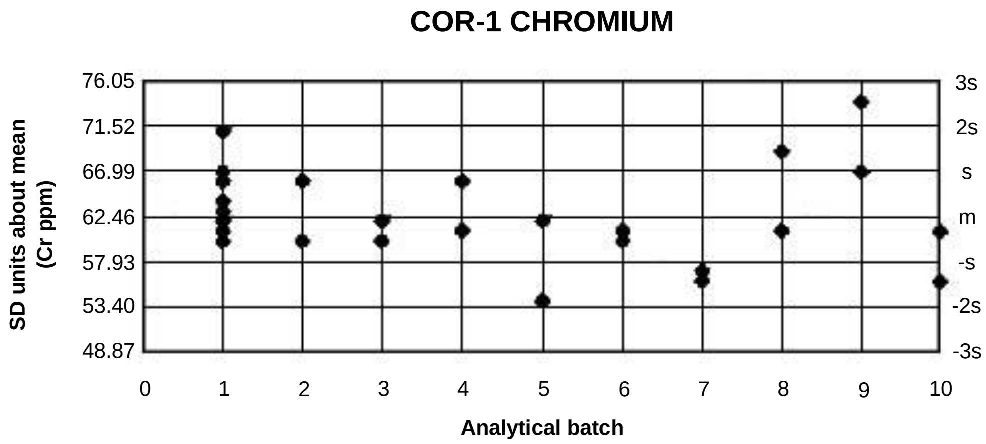


Figure 5. Control charts for Calcium





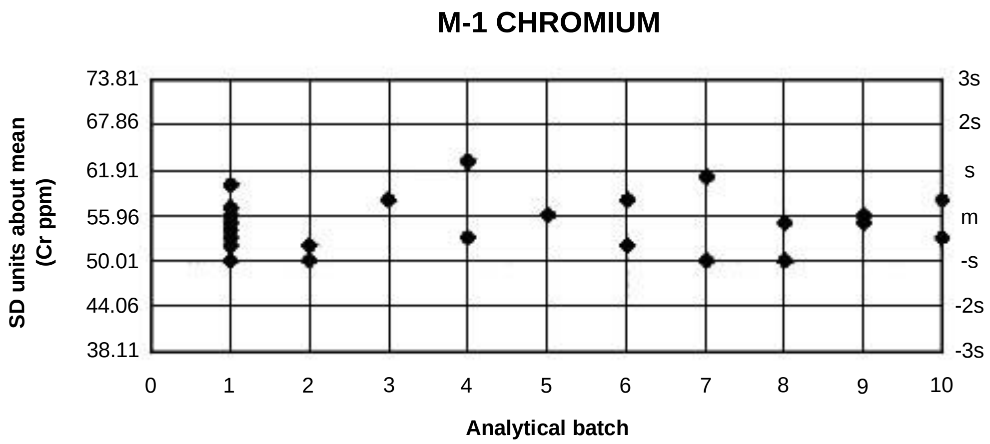
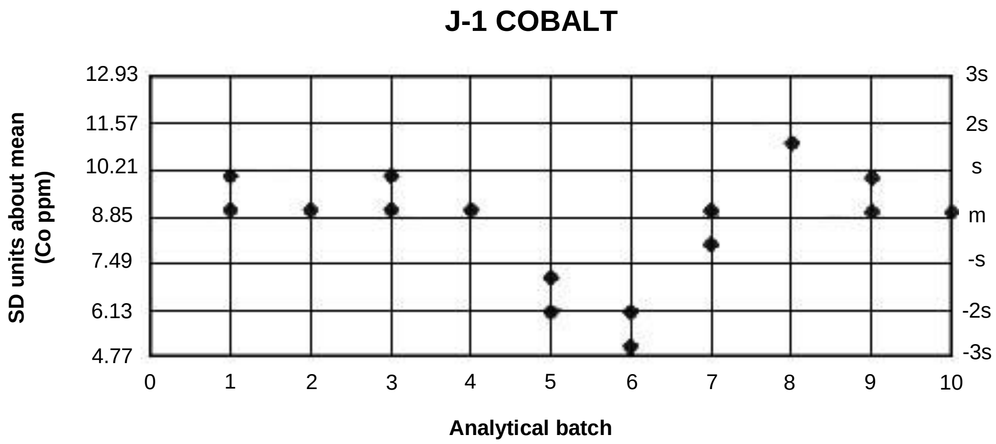
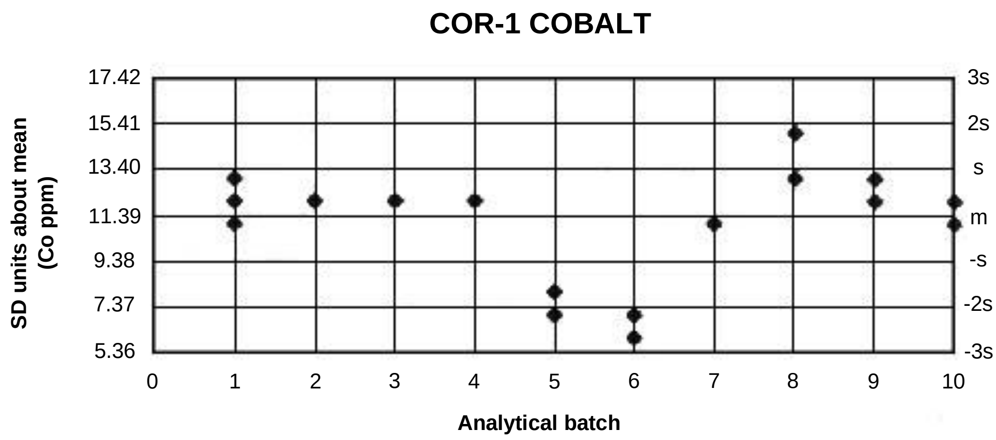


Figure 6. Control charts for Chromium





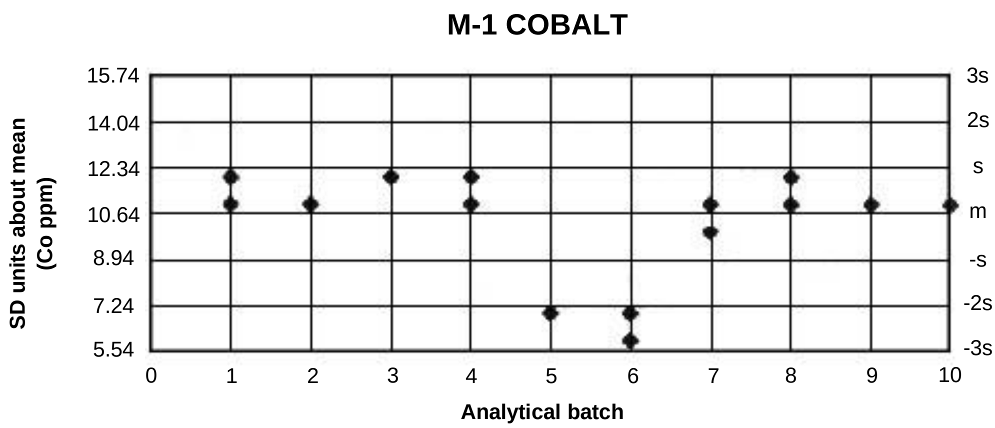
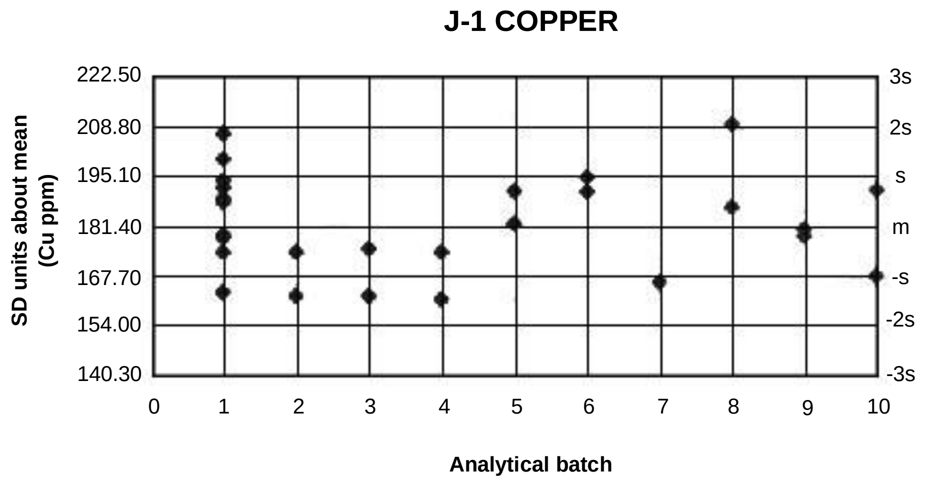
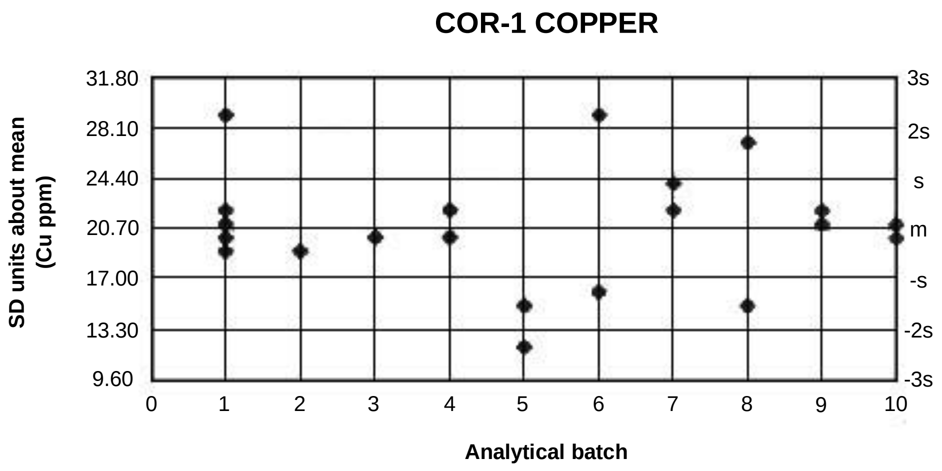


Figure 7. Control charts for Cobalt





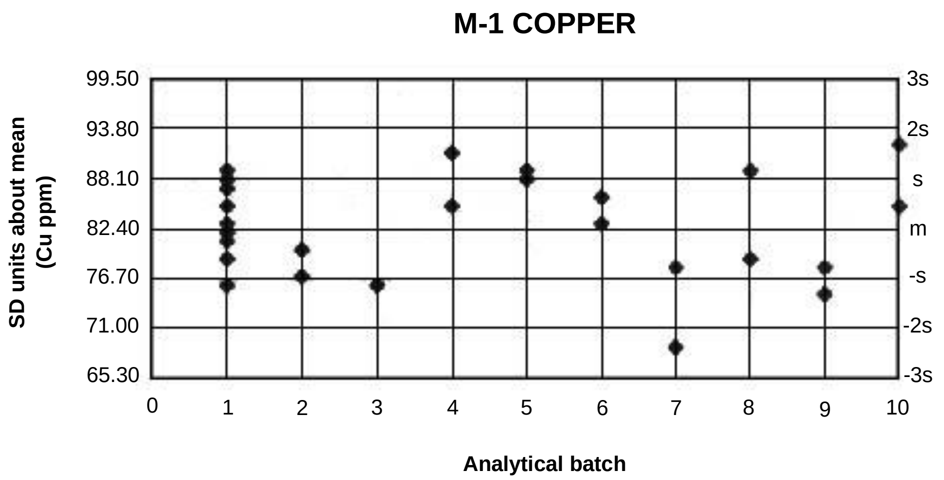
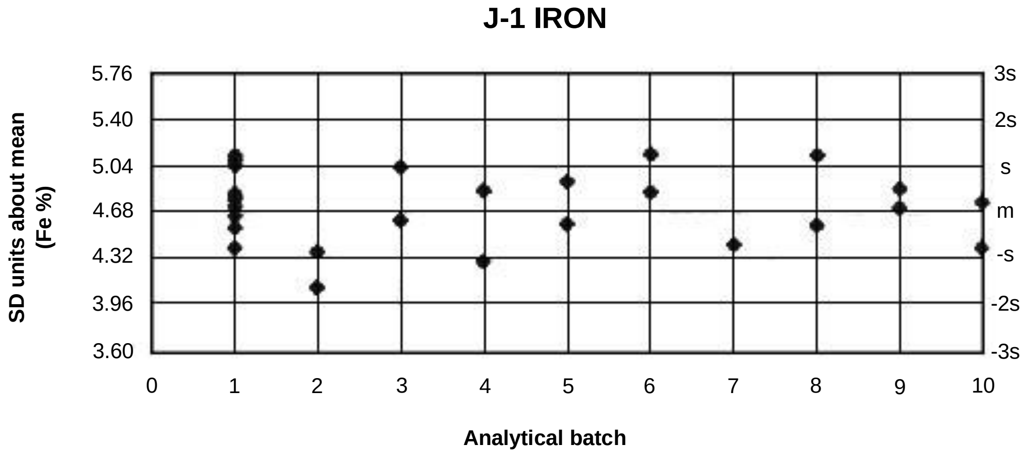
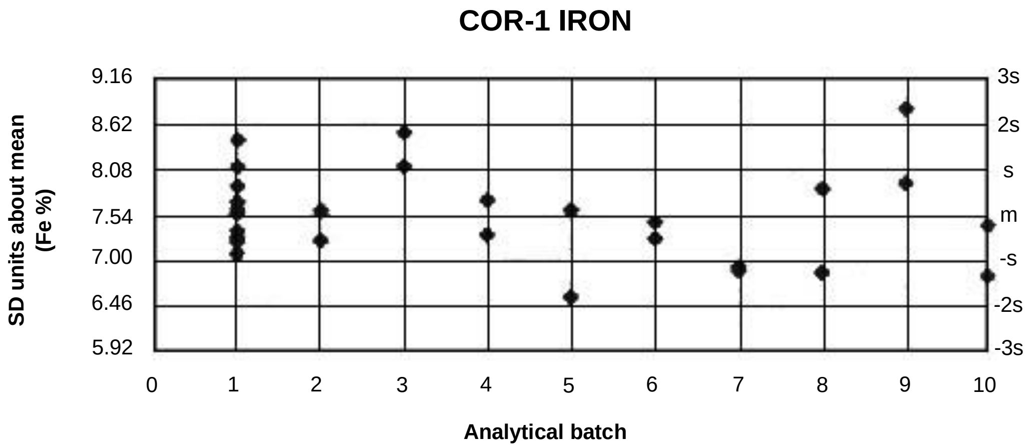


Figure 8. Control charts for Copper





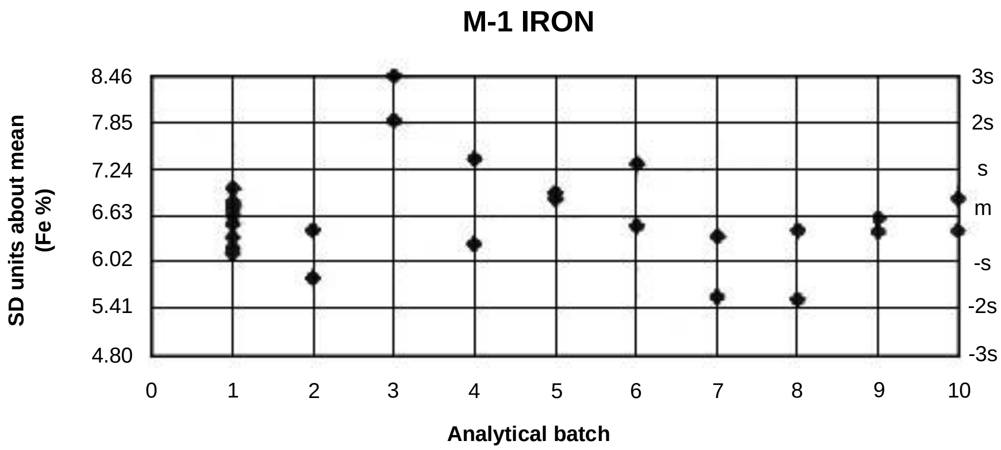
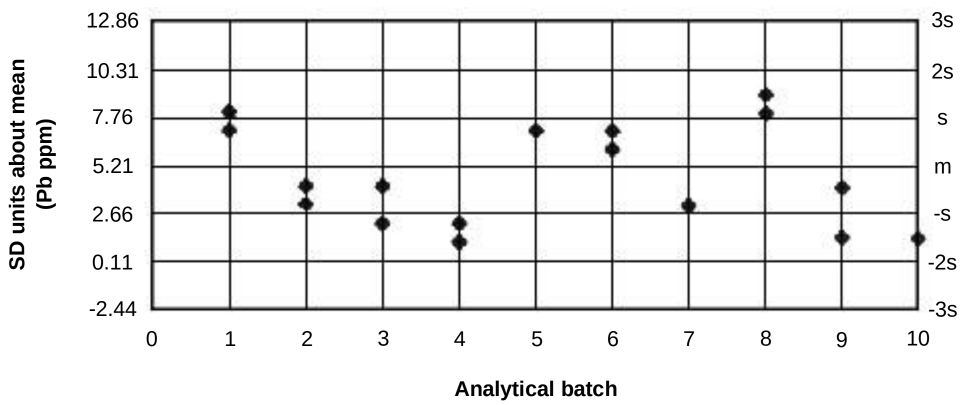
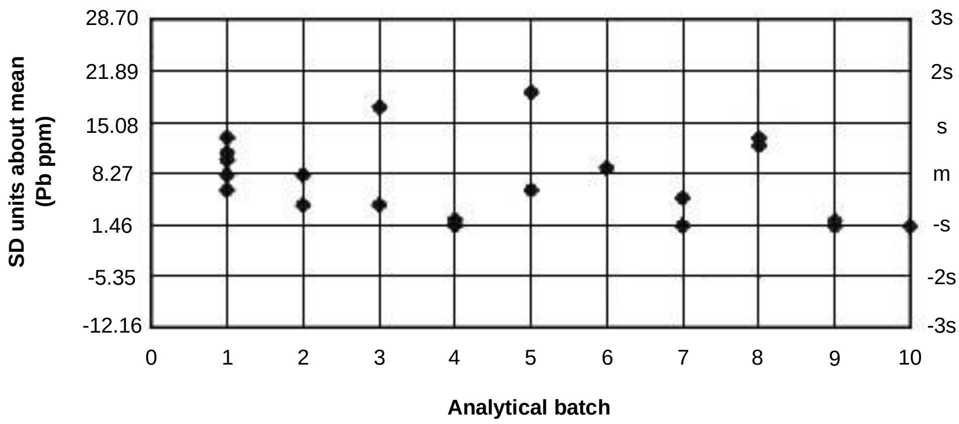


Figure 9. Control charts for Iron

J-1 LEAD



COR-1 LEAD



M-1 LEAD

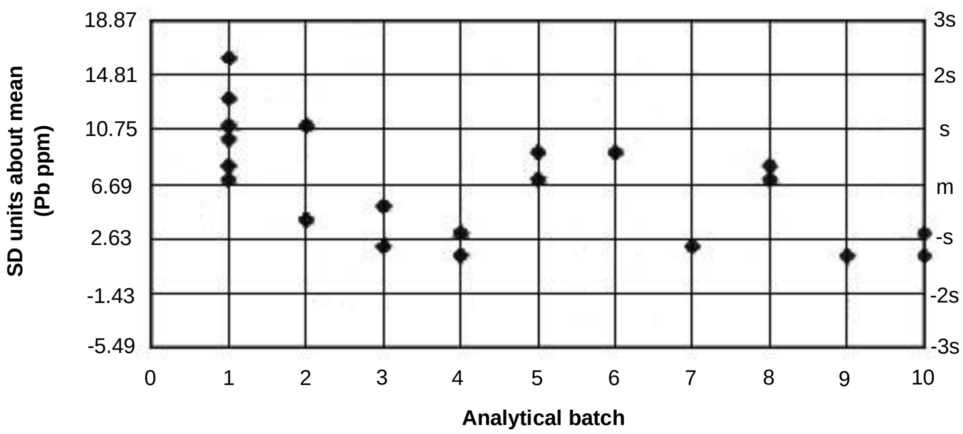
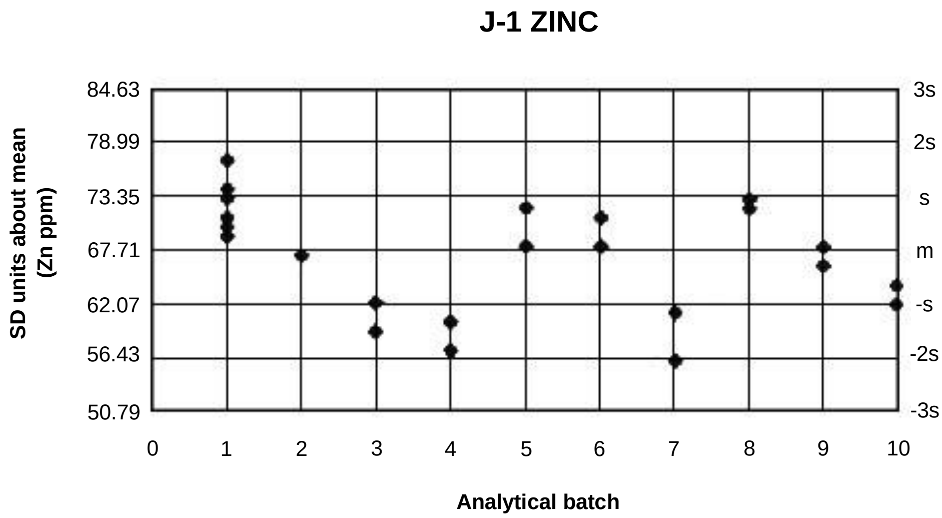
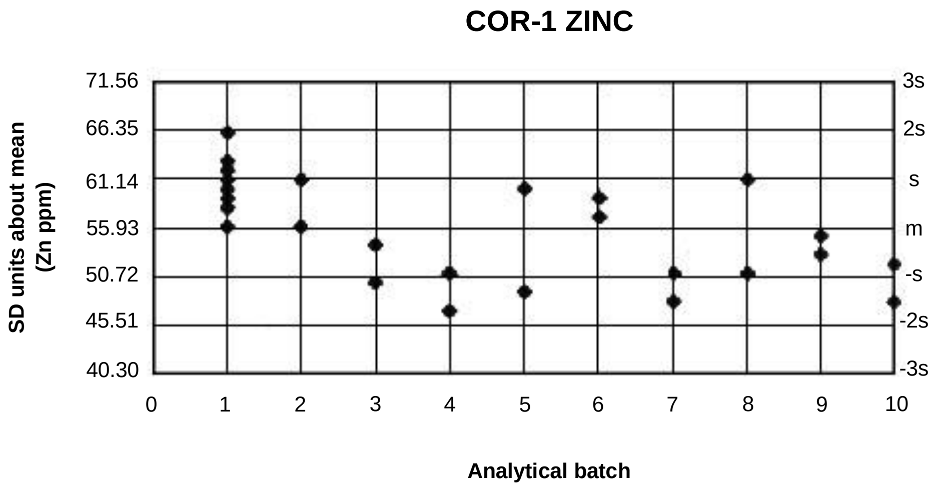


Figure 10. Control charts for Lead





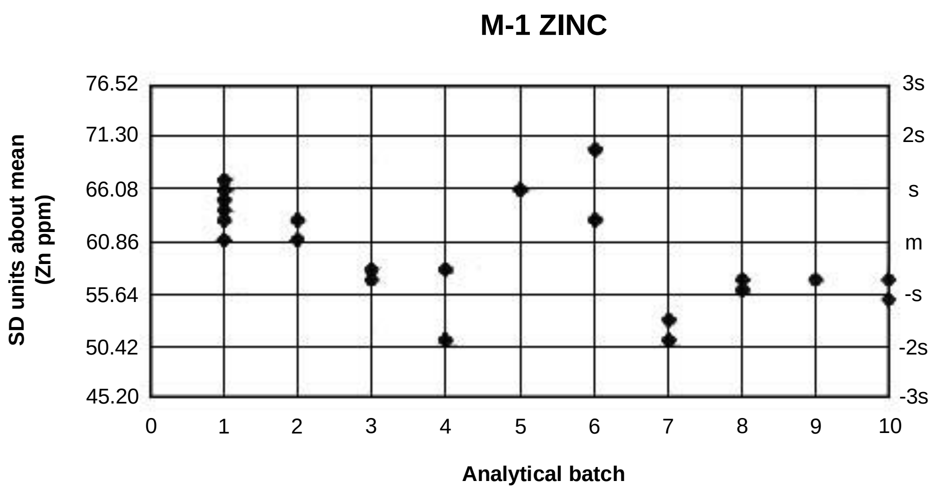
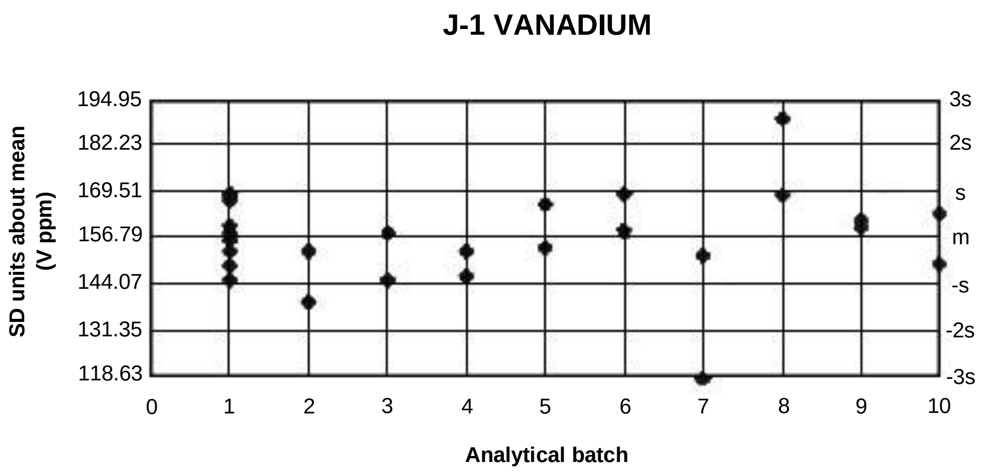
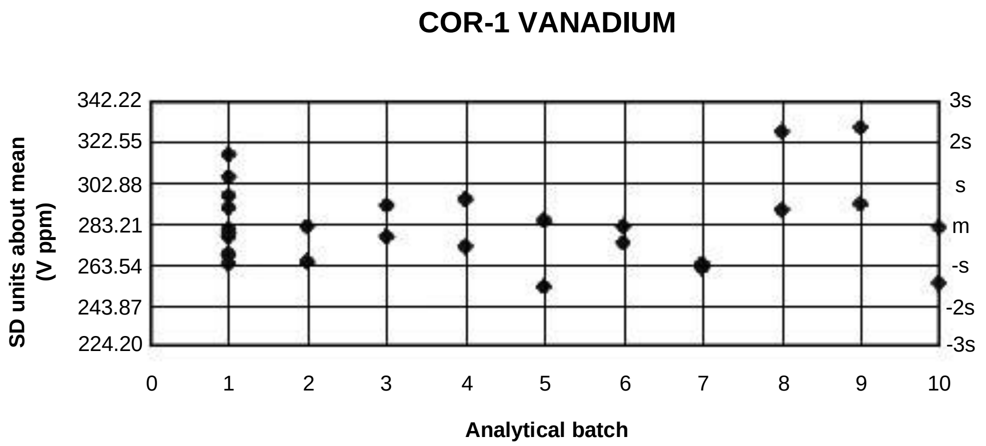


Figure 11. Control charts for Zinc





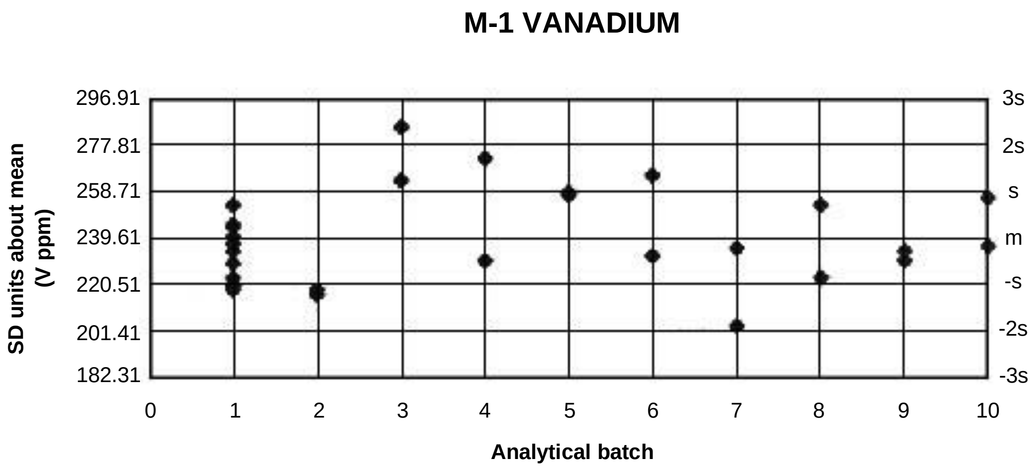
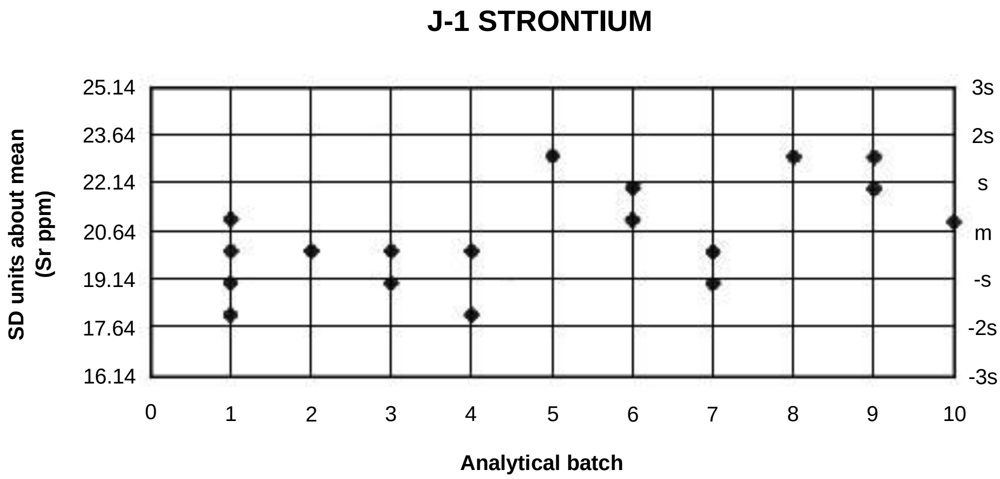
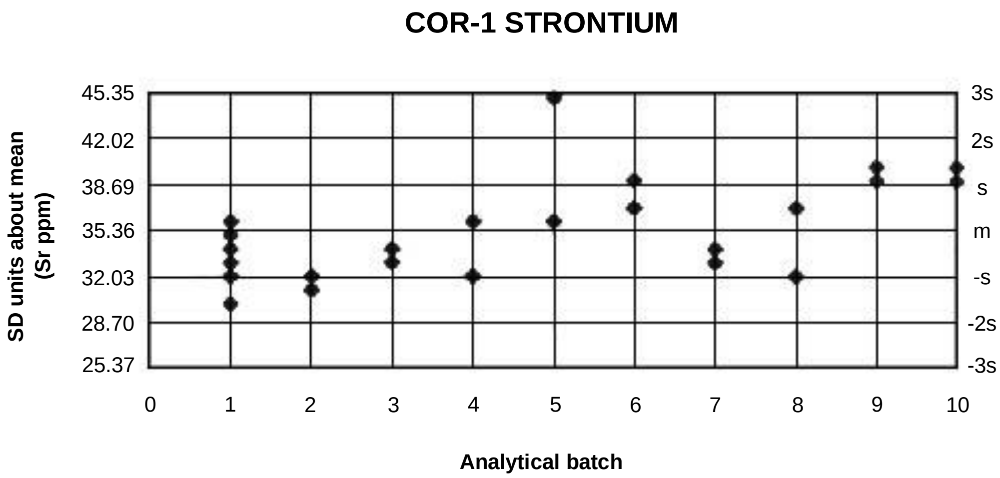


Figure 12. Control charts for Vanadium





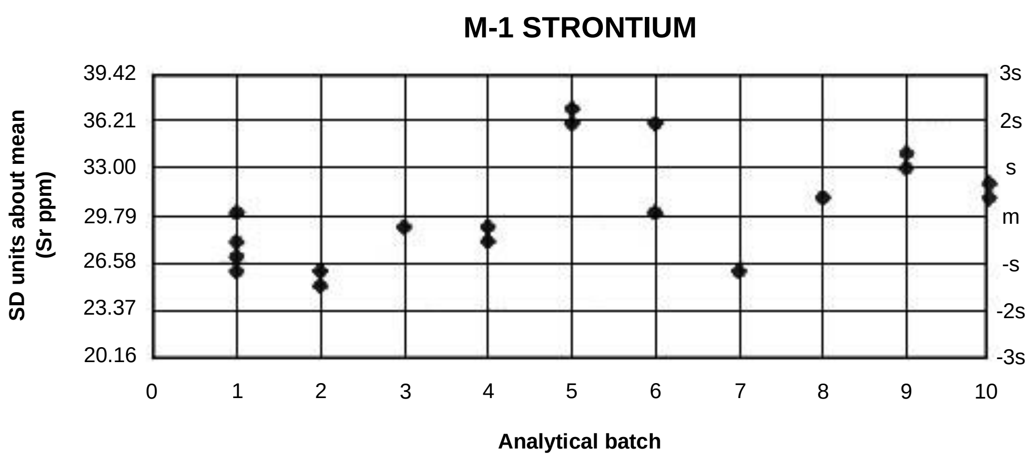
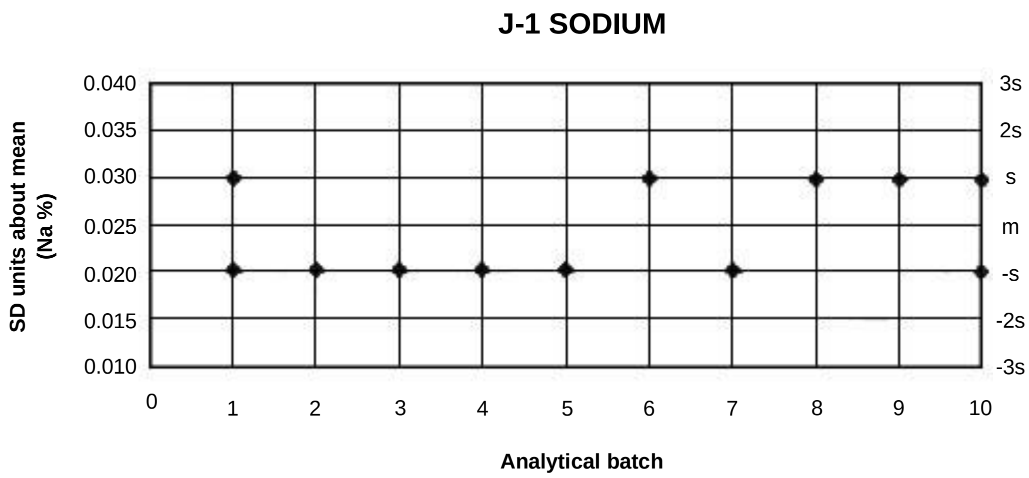
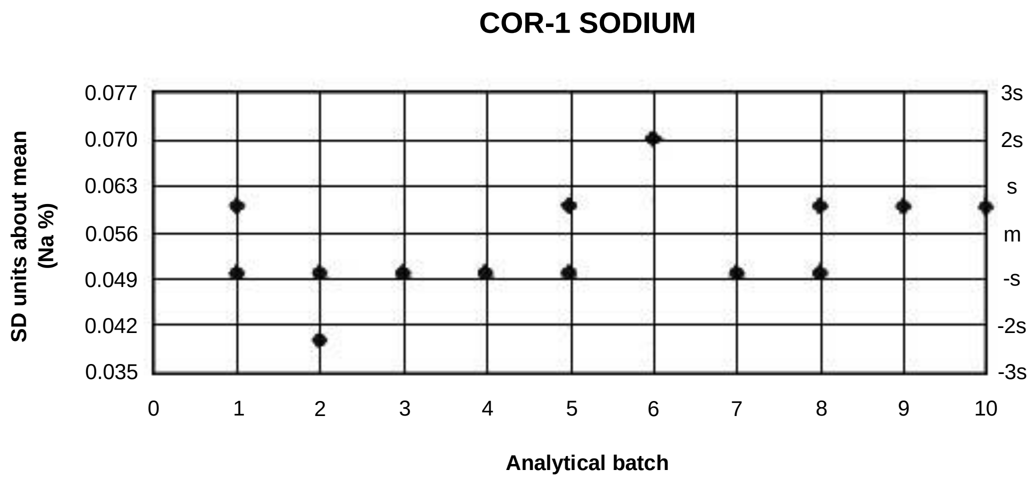


Figure 13. Control charts for Strontium





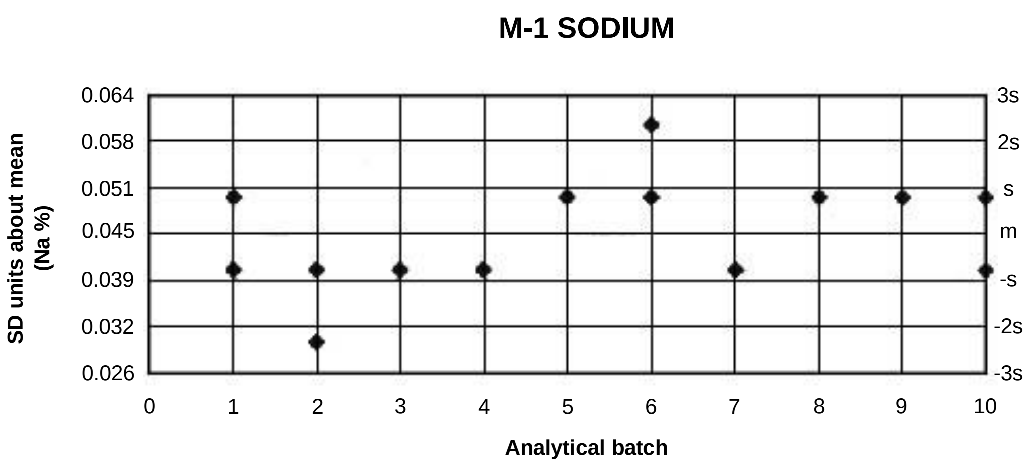
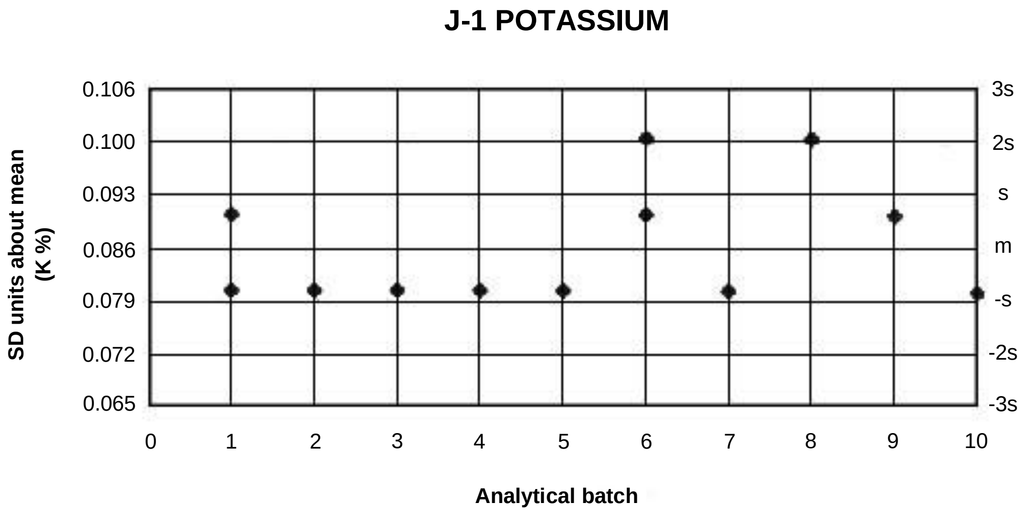
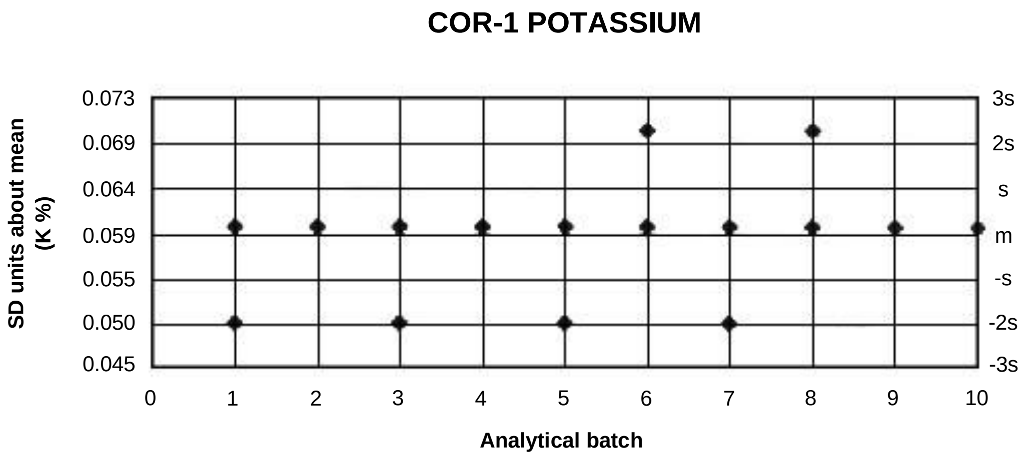


Figure 14. Control charts for Sodium





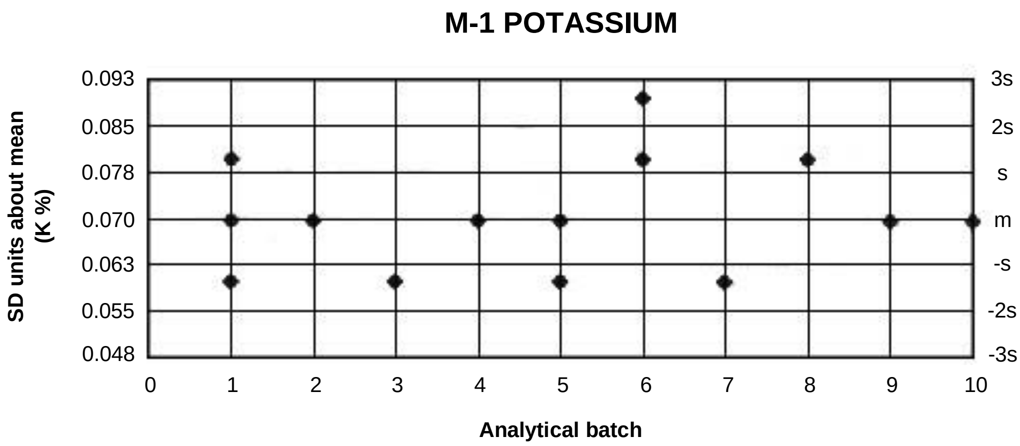
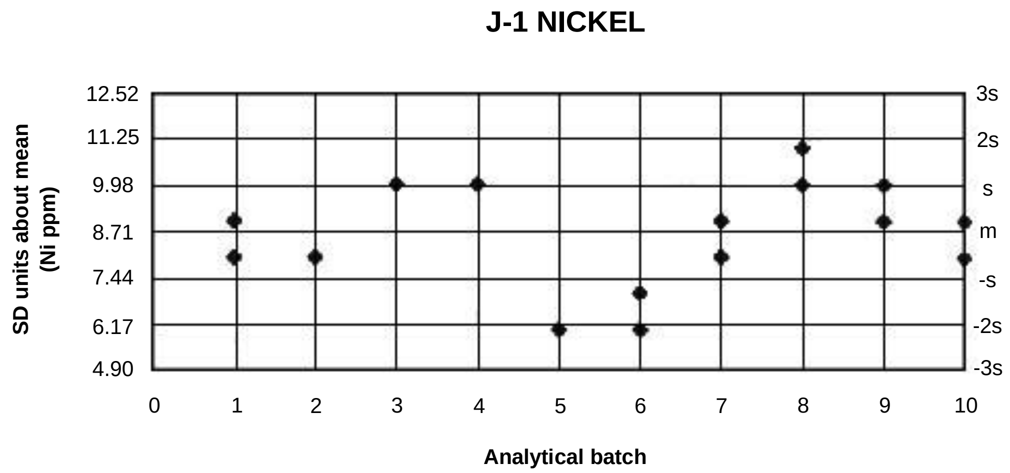
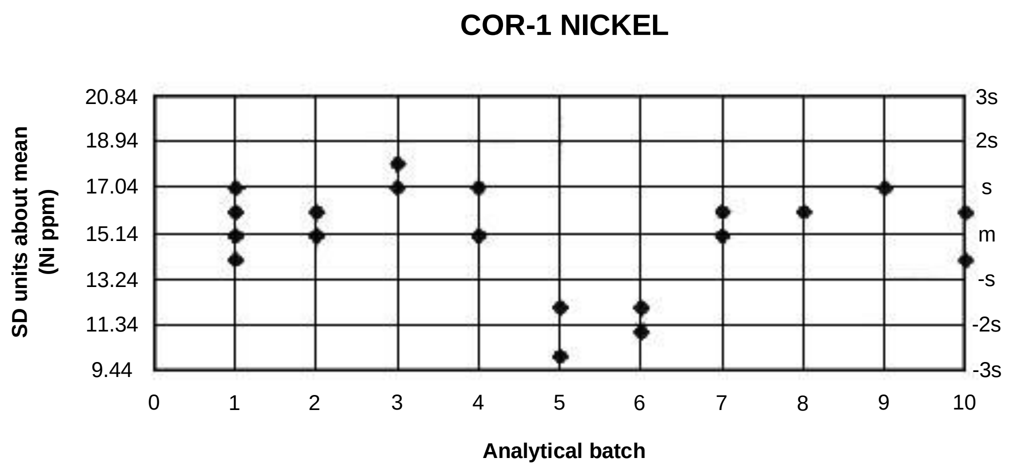


Figure 15. Control charts for Potassium





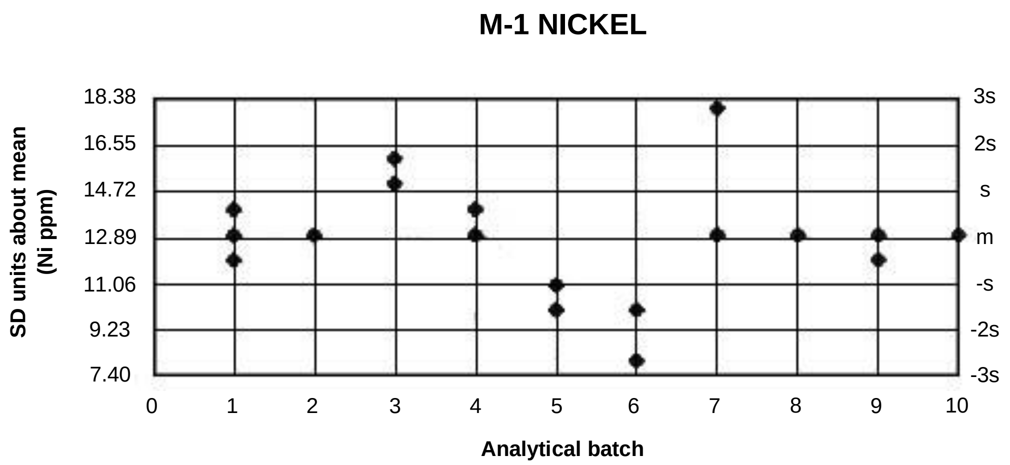
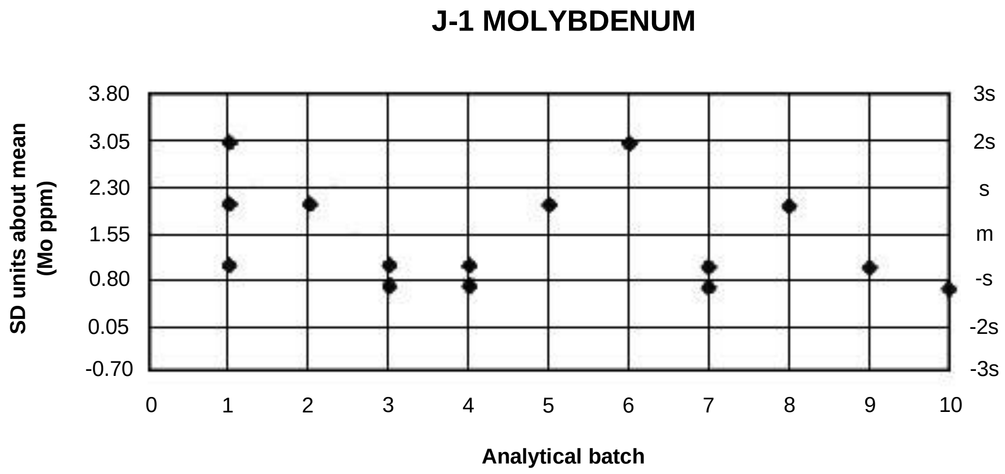
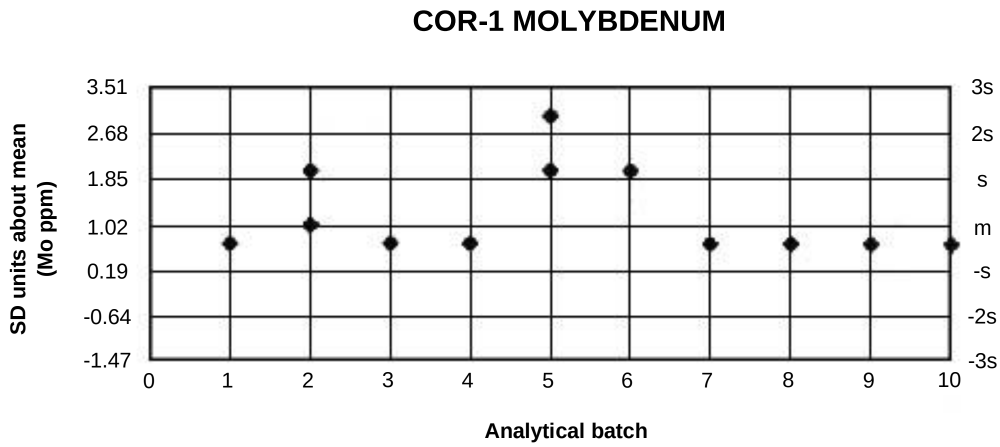


Figure 16. Control charts for Nickel





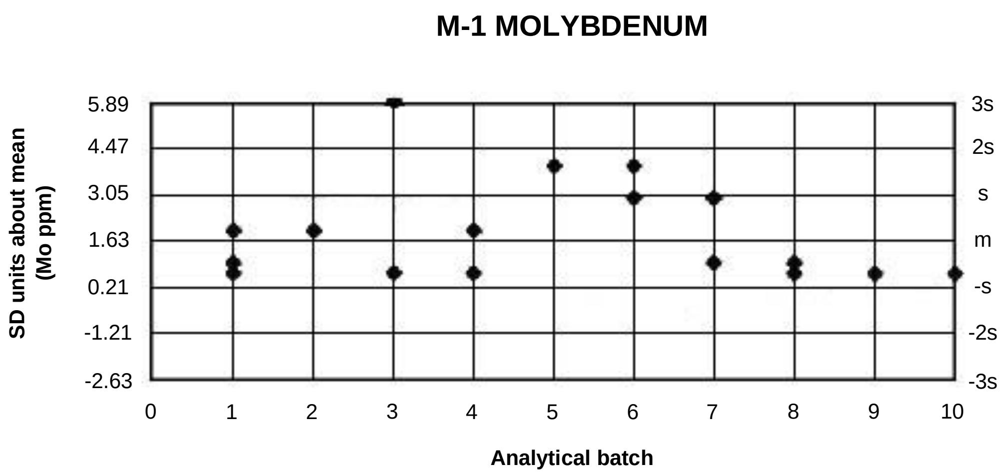
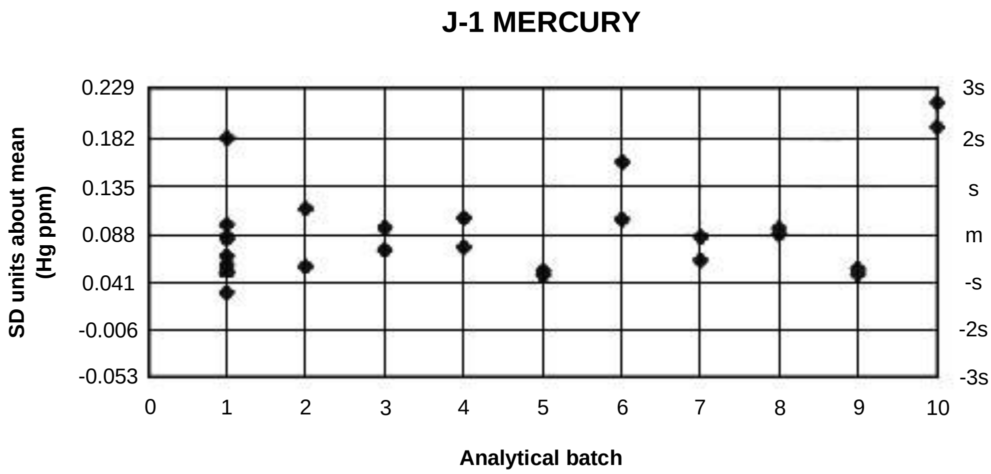
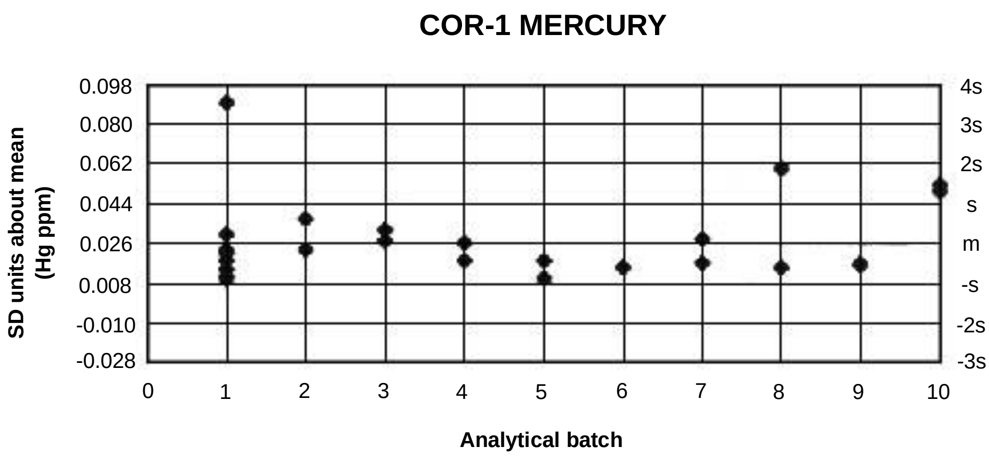


Figure 17. Control charts for Molybdenum





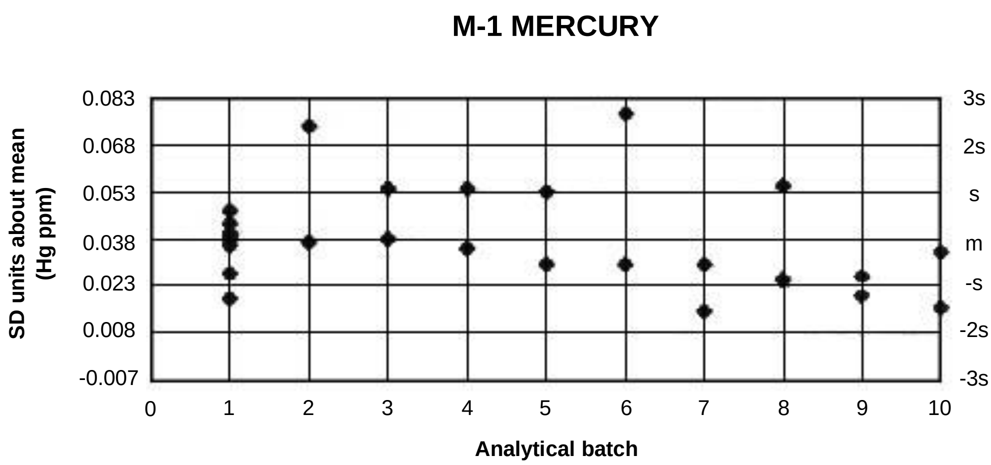
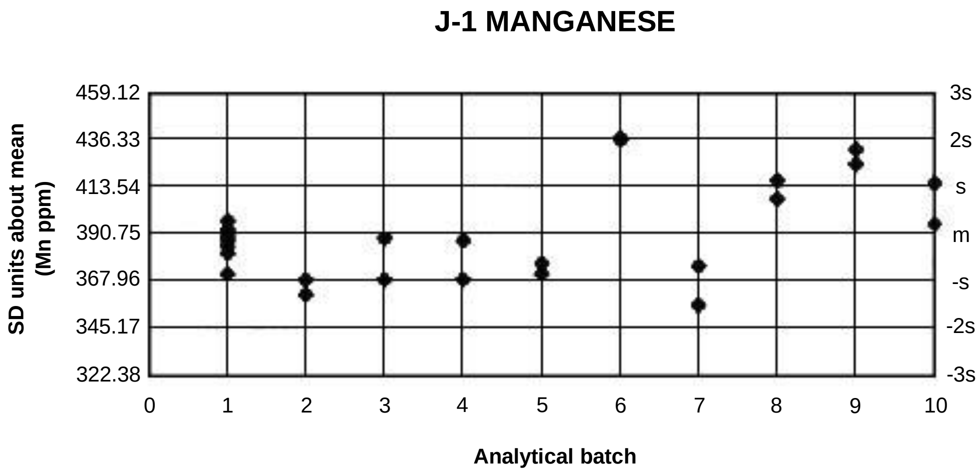
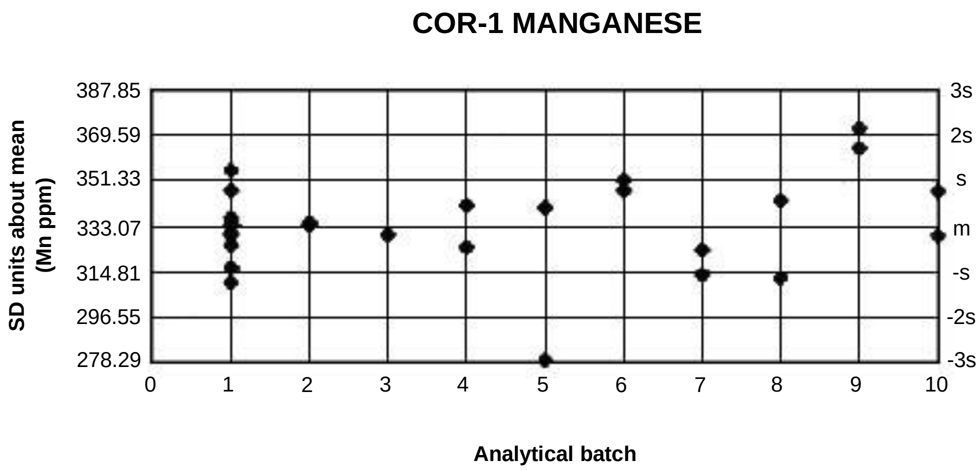


Figure 18. Control charts for Mercury





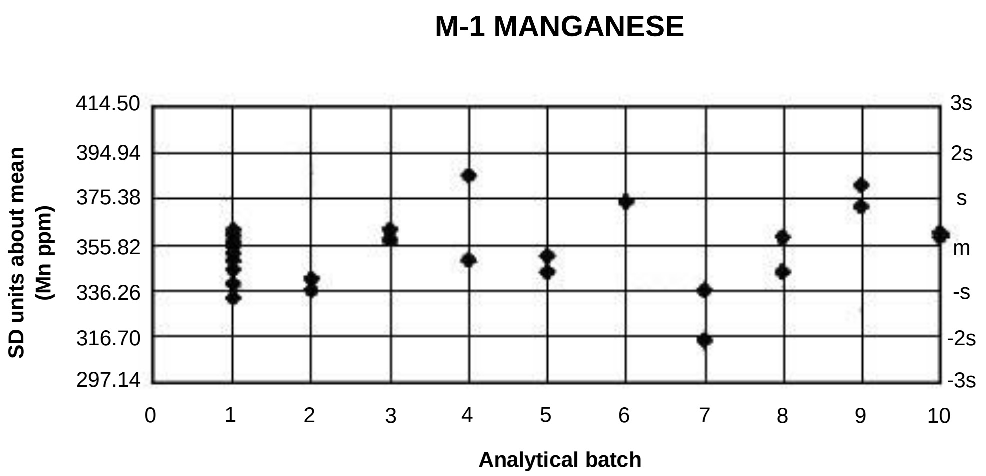
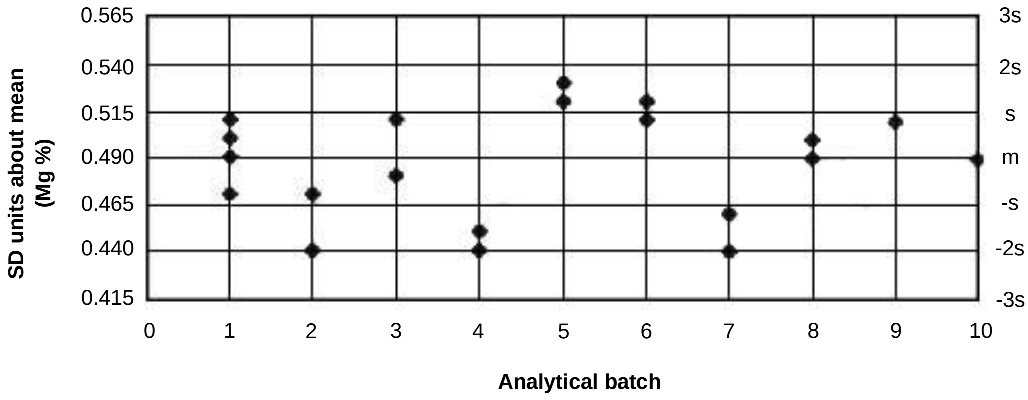
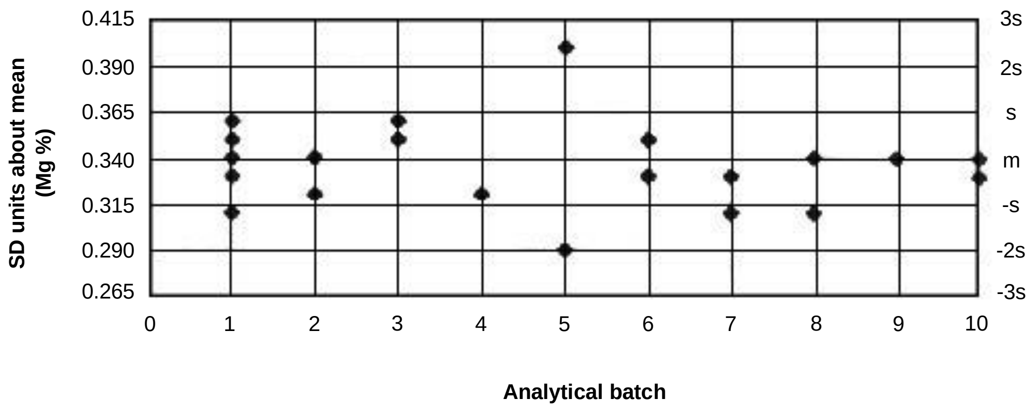


Figure 19. Control charts for Manganese

J-1 MAGNESIUM



COR-1 MAGNESIUM



M-1 MAGNESIUM

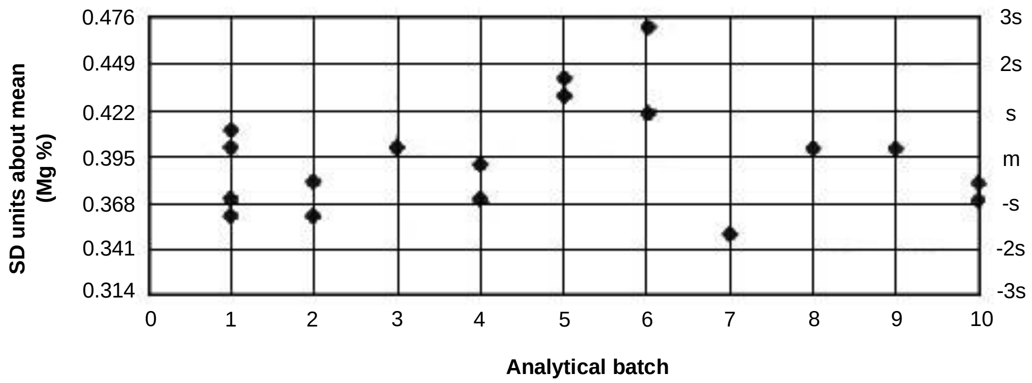
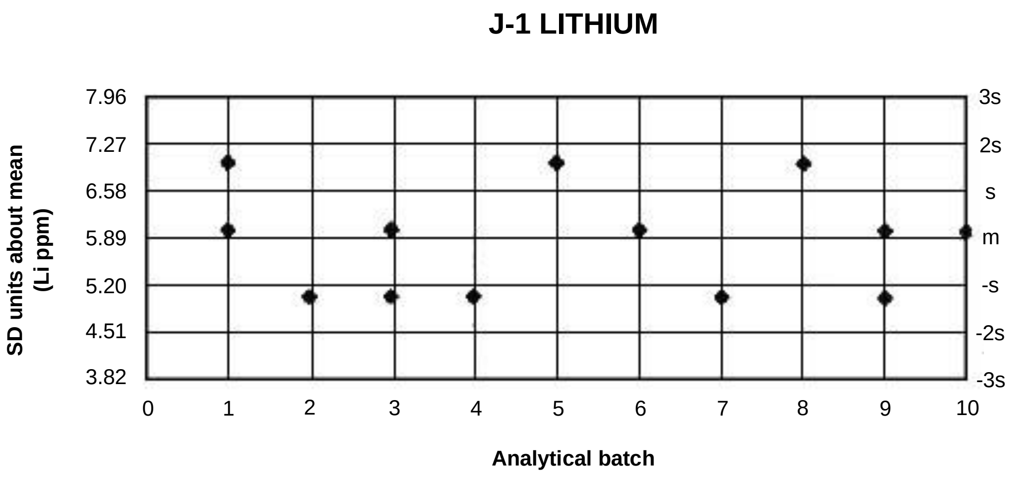
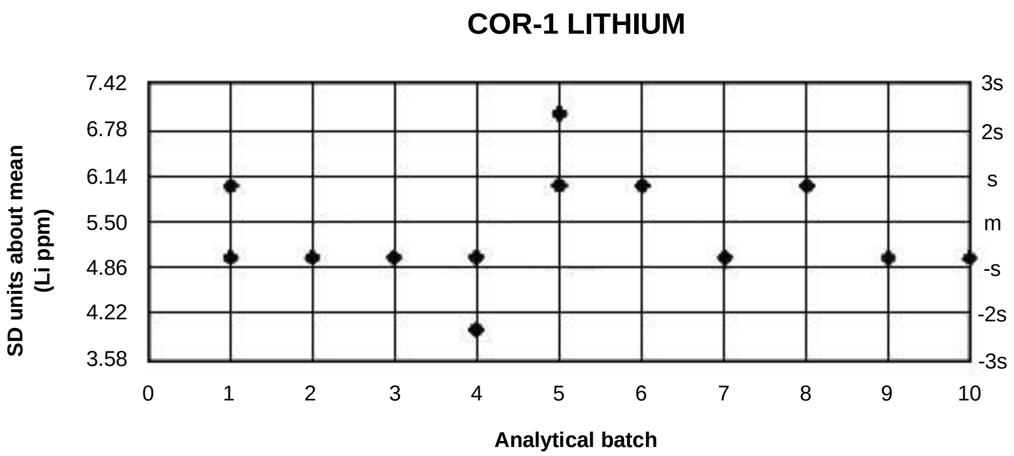


Figure 20. Control charts for Magnesium





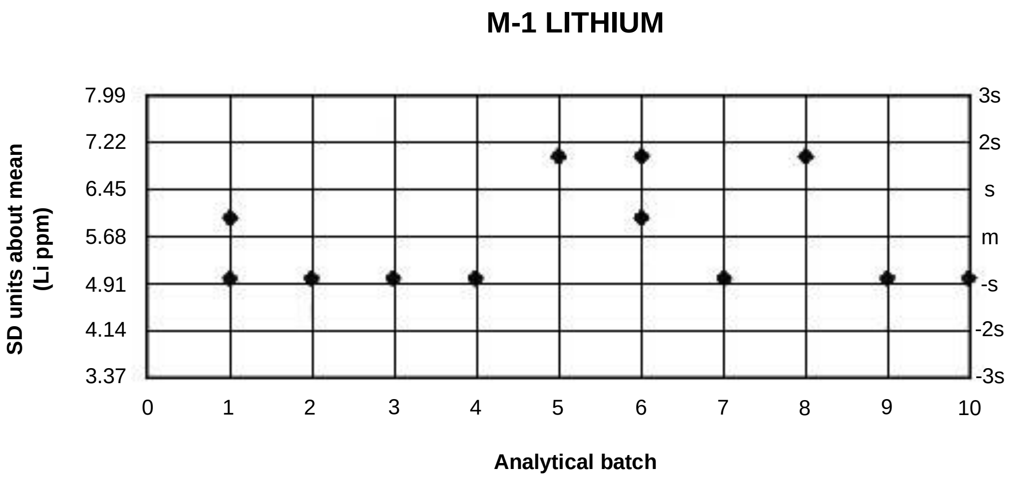
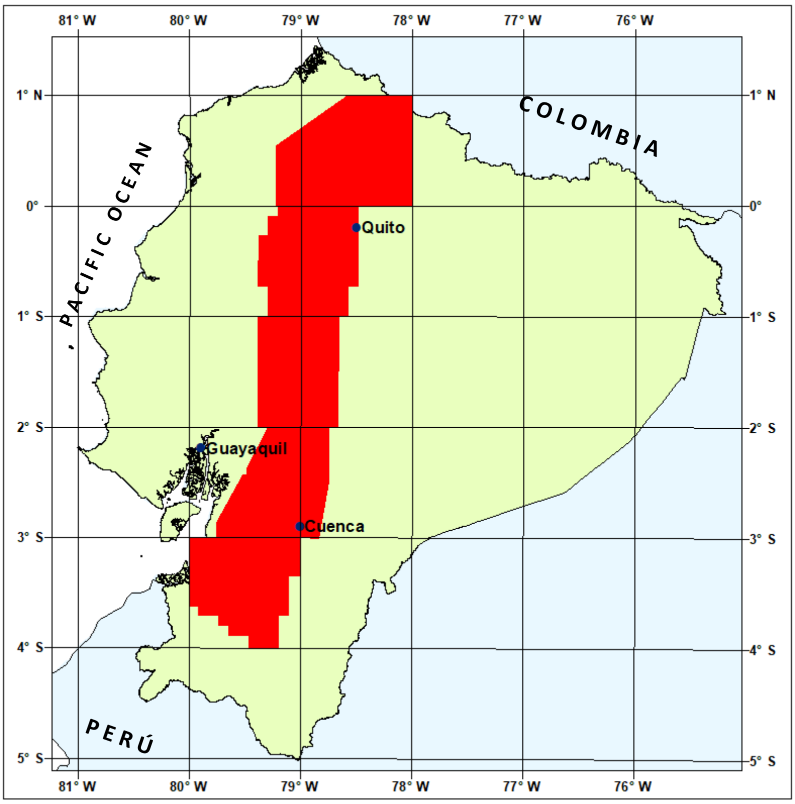


Figure 21. Control charts for Lithium

APPENDIX 3 OF REPORT:

CONTROL OF QUALITY OF GEOCHEMICAL DATA

ORIGINAL AND DUPLICATE ANALYSES SCATTER PLOTS



GEOLOGICAL INFORMATION MAPPING PROGRAMME

QUITO, 1997

Scatter plots showing original analyses plotted against repeat analyses

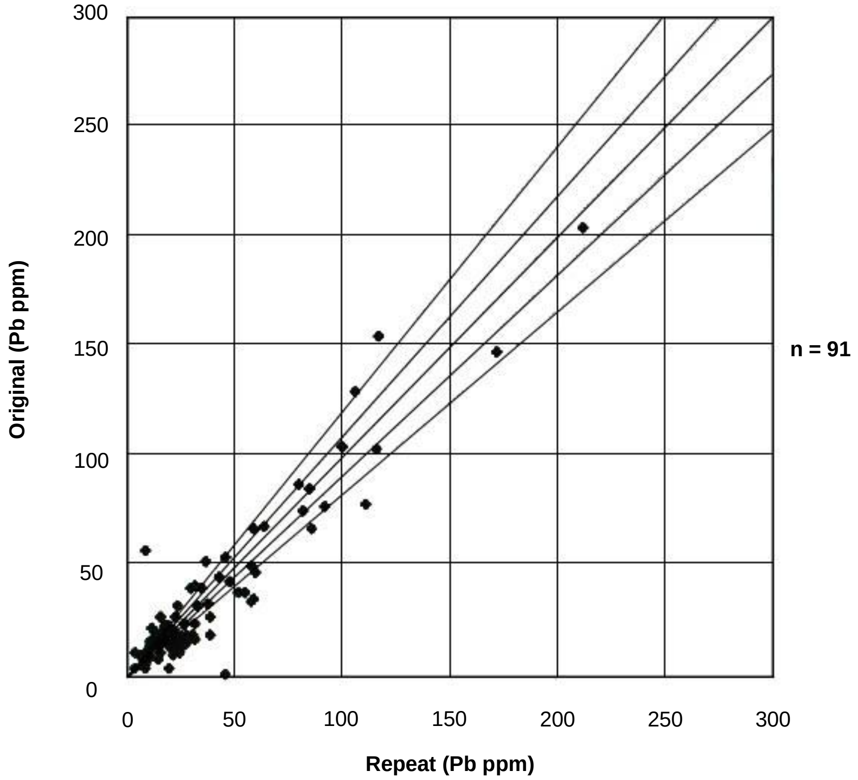


Figure 1. Lead original vs repeat analyses

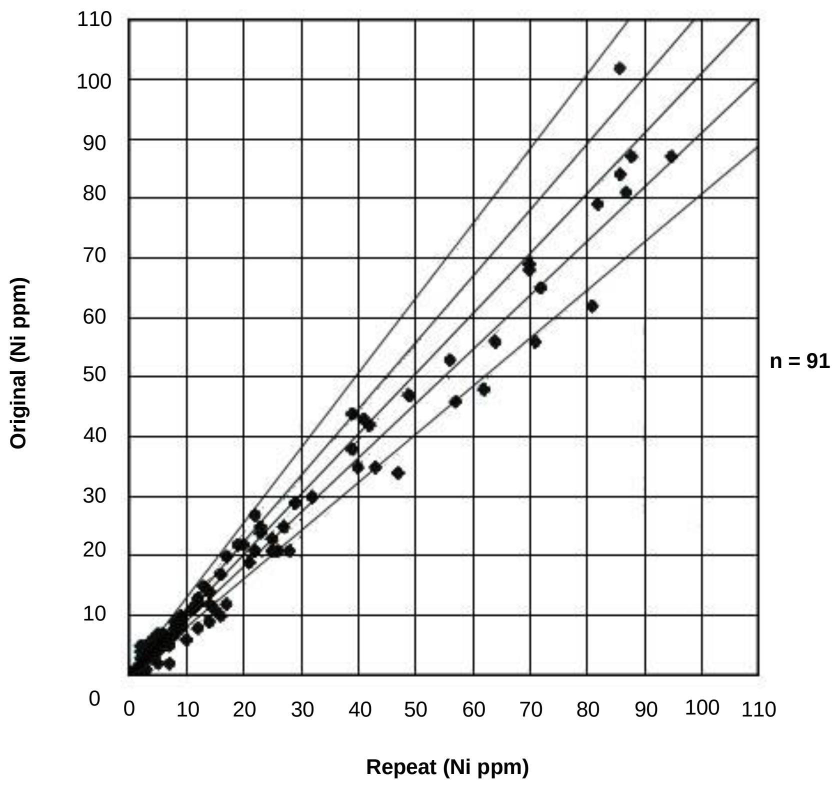


Figure 2. Nickel original vs repeat analyses

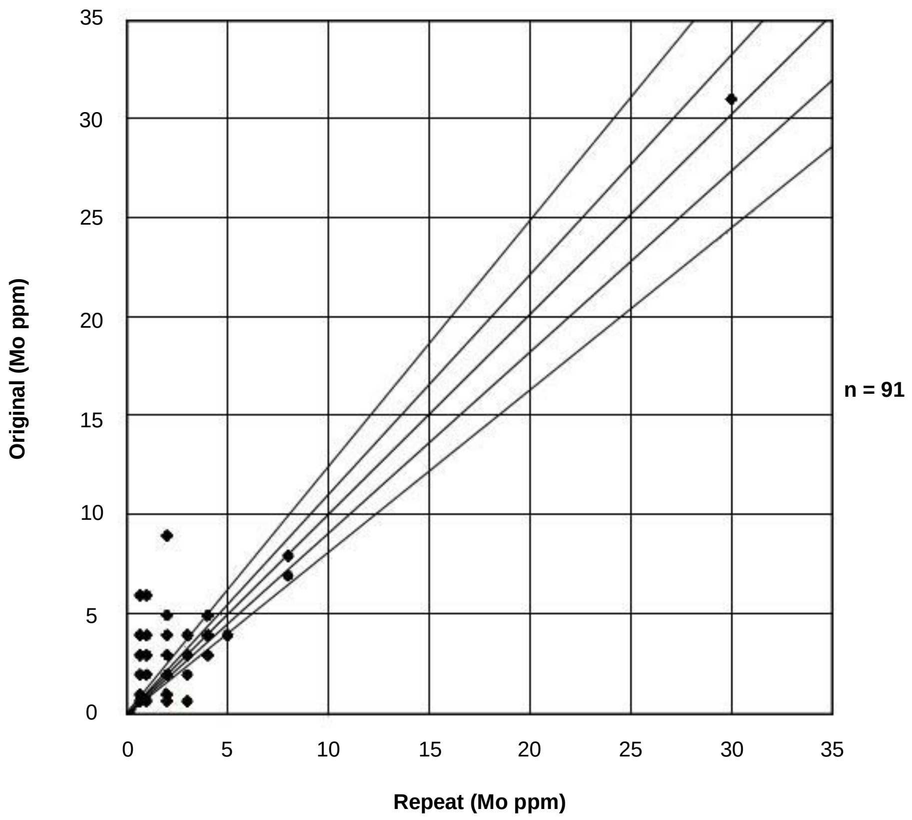


Figure 3. Molybdenum original vs repeat analyses

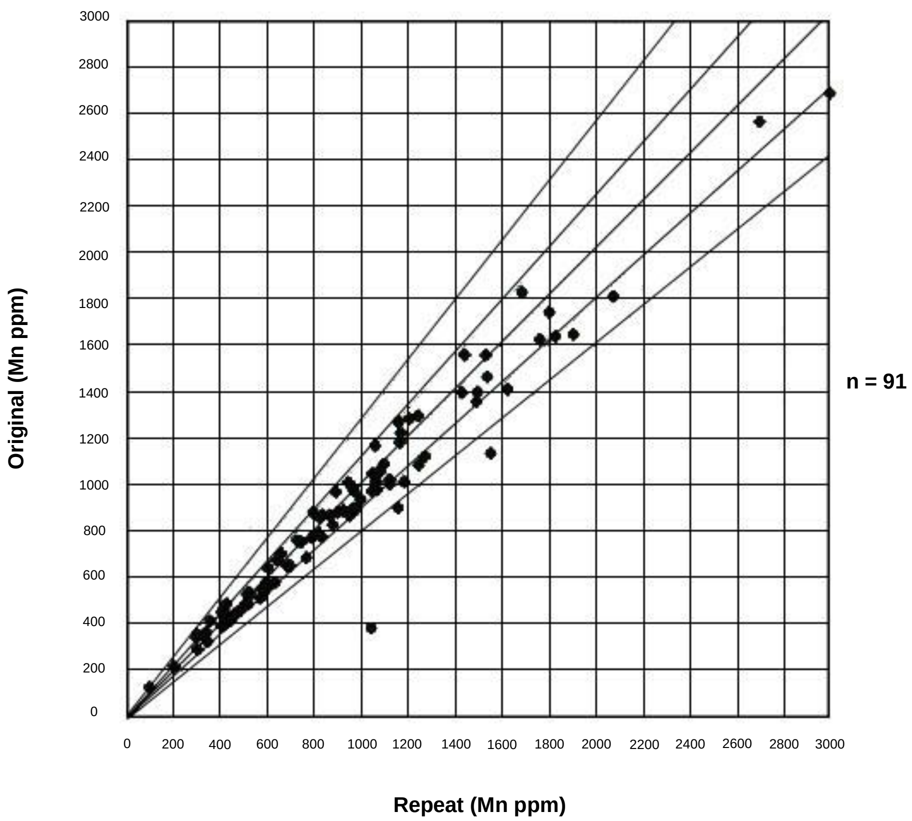


Figure 4. Manganese original vs repeat analyses

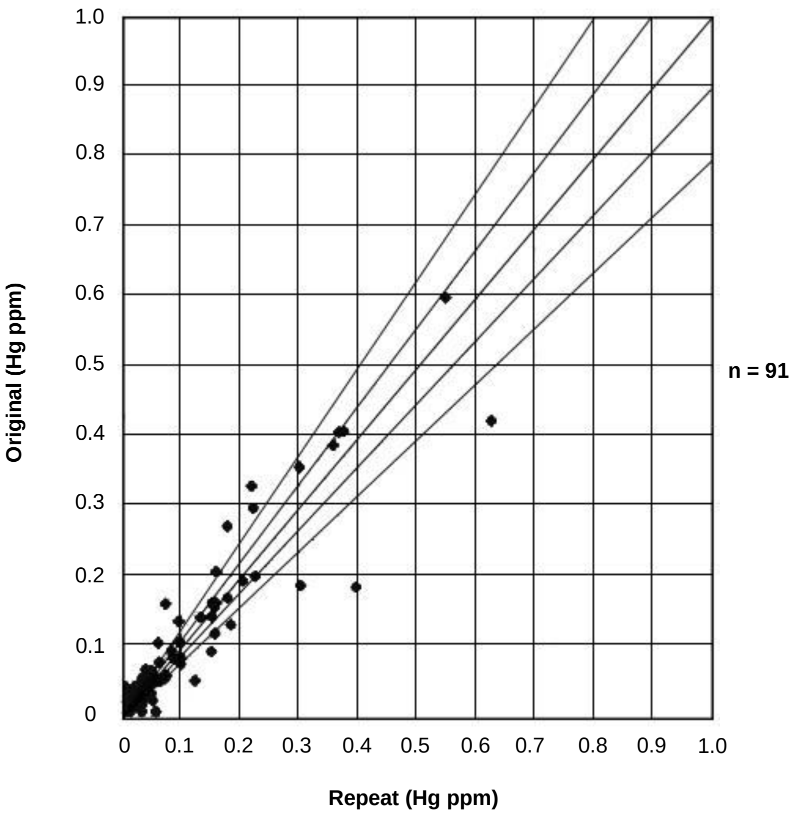


Figure 5. Mercury original vs repeat analyses

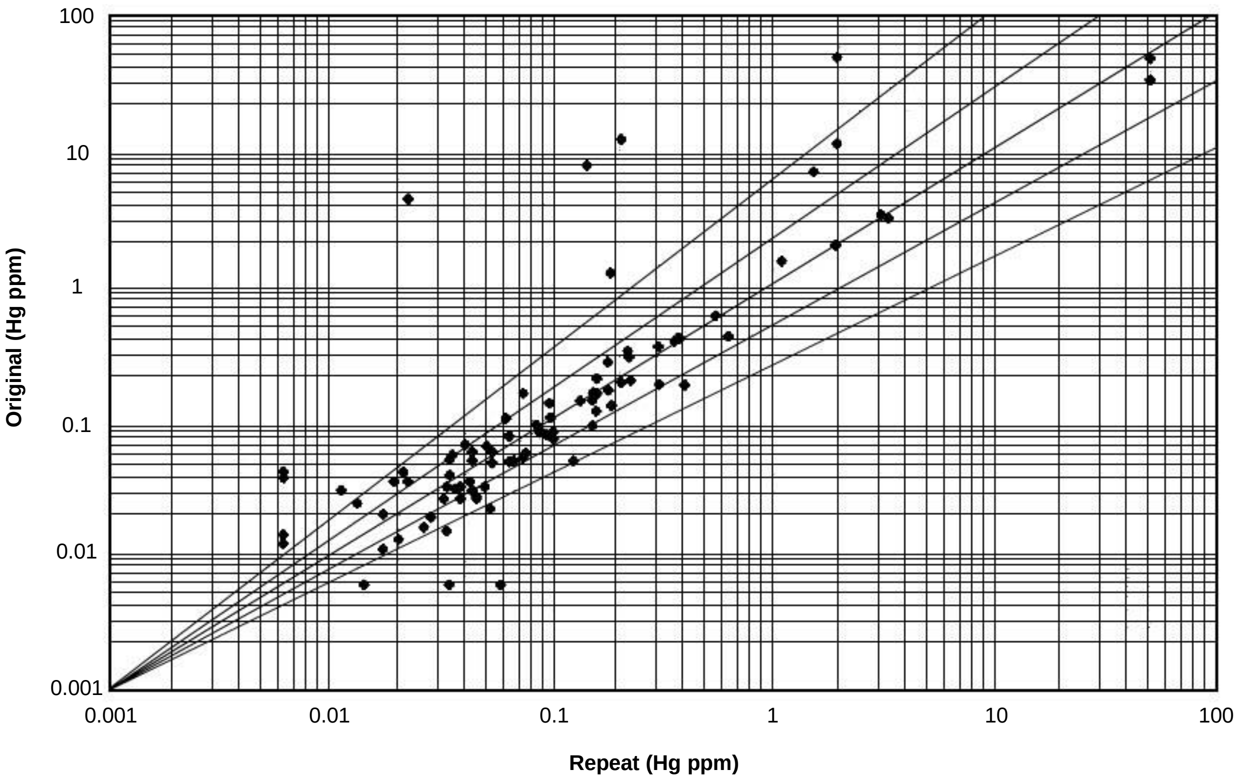


Figure 6. Mercury original vs repeat analyses

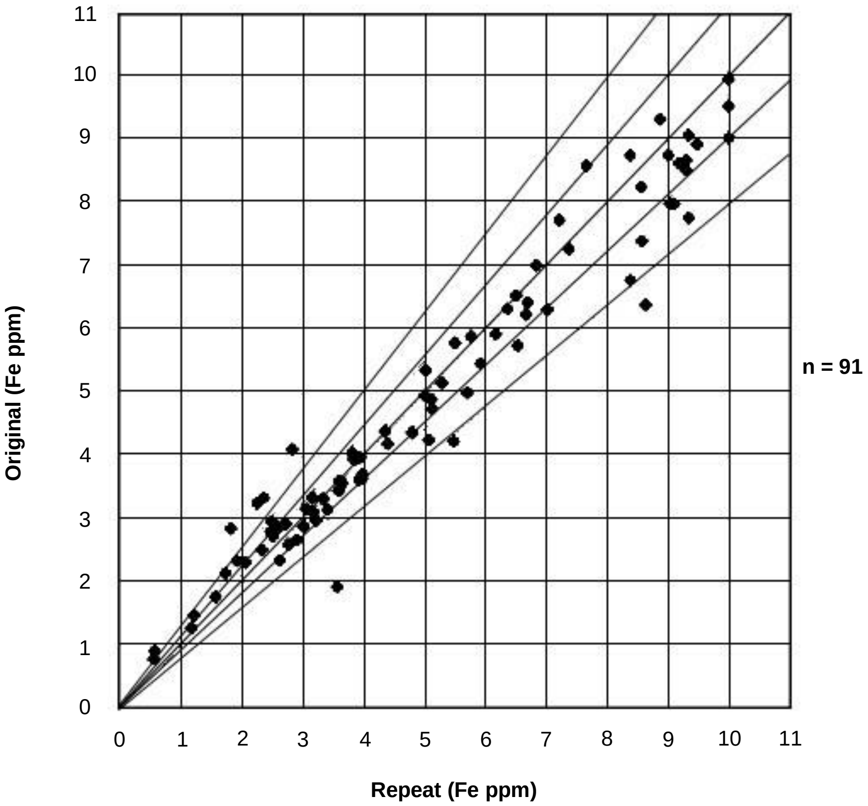


Figure 7. Iron original vs repeat analyses

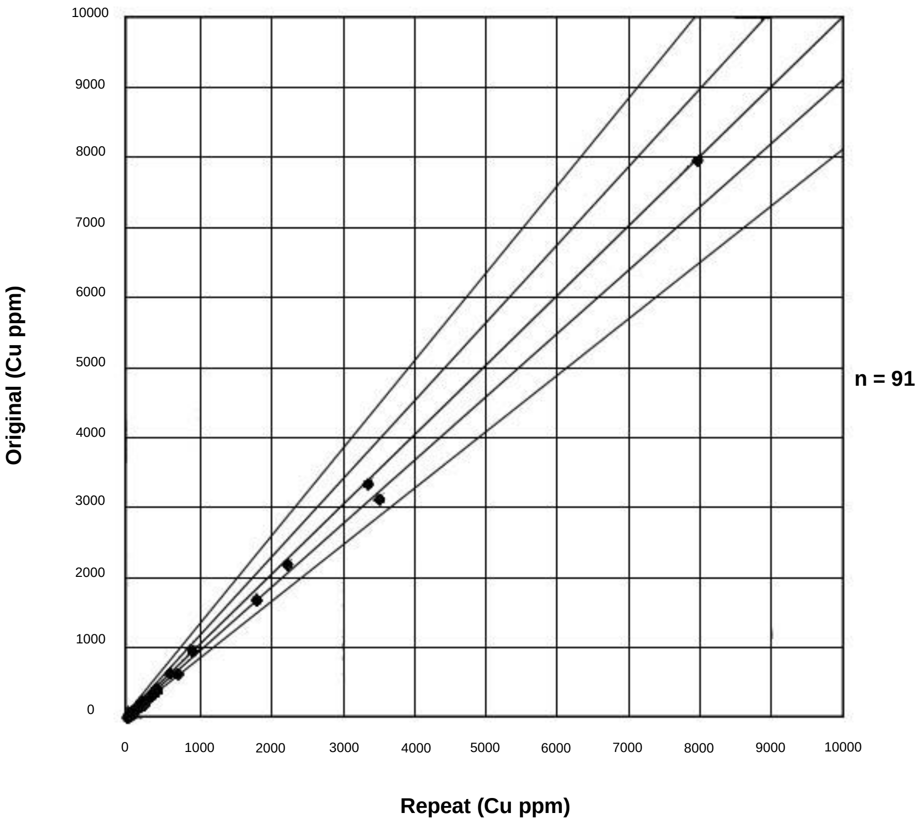


Figure 8. Copper original vs repeat analyses

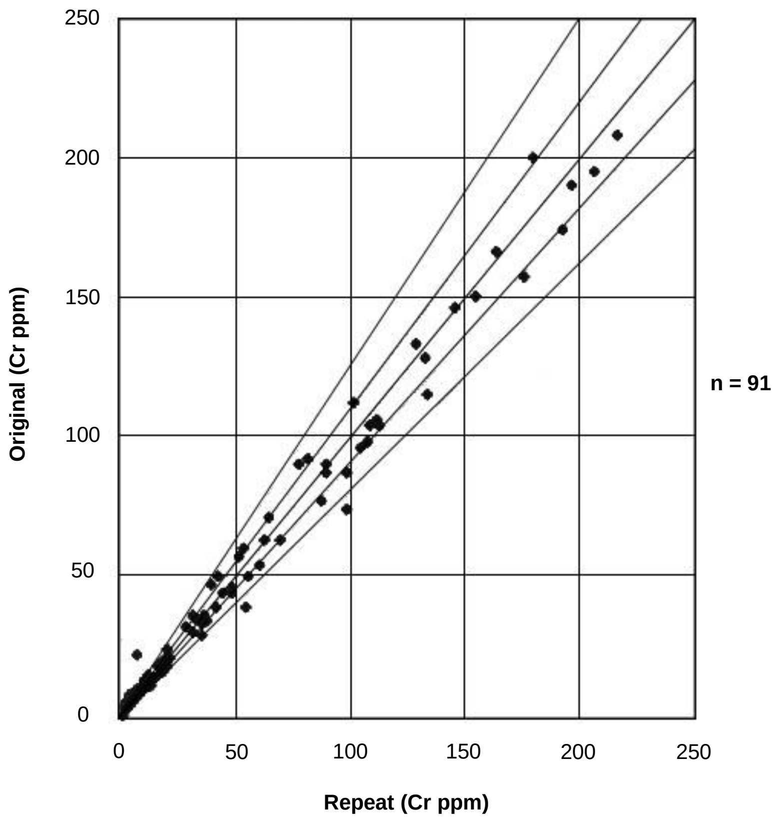


Figure 9. Chromium original vs repeat analyses

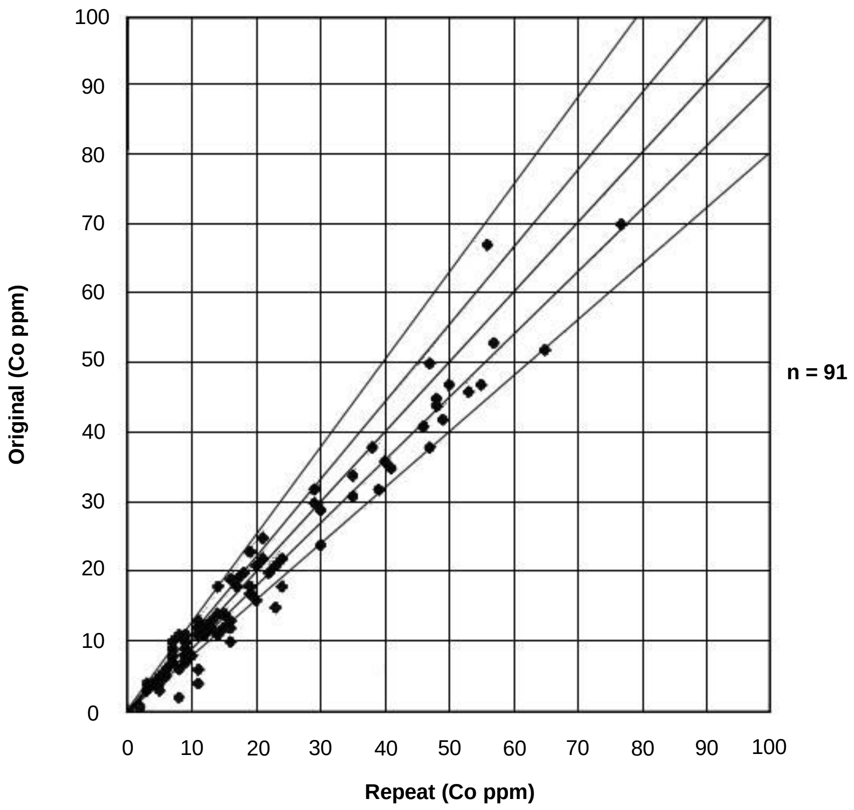


Figure 10. Cobalt original vs repeat analyses

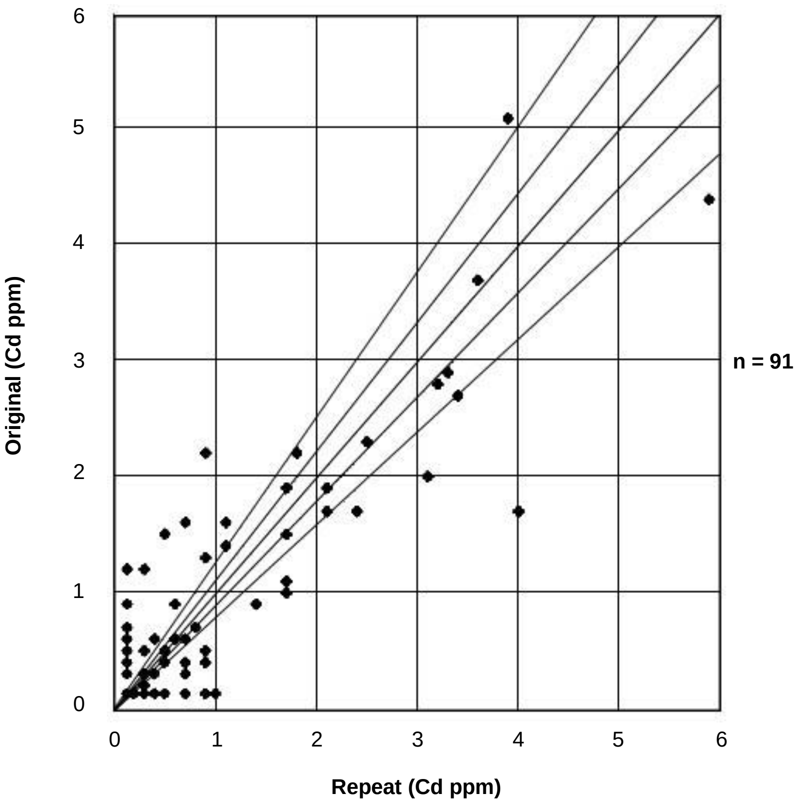


Figure 11. Cadmium original vs repeat analyses

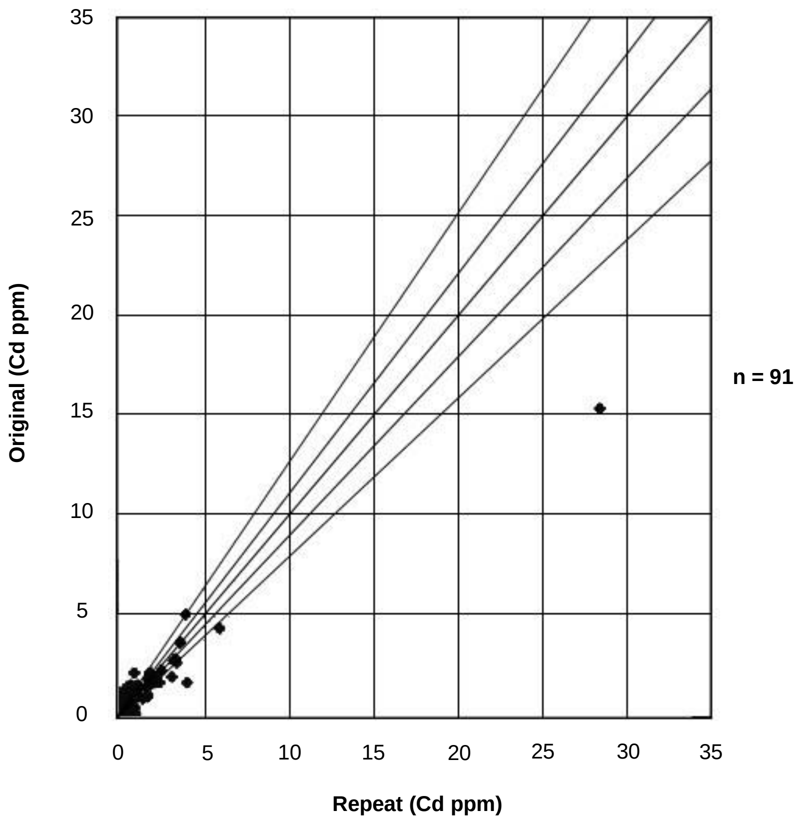


Figure 12. Cadmium original vs repeat analyses

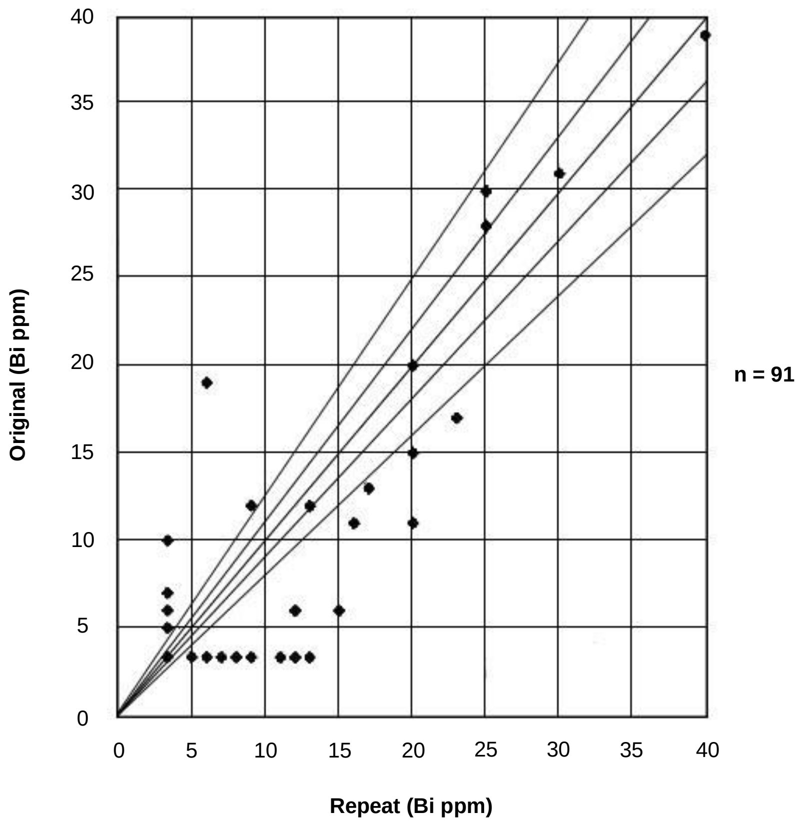


Figure 13. Bismuth original vs repeat analyses

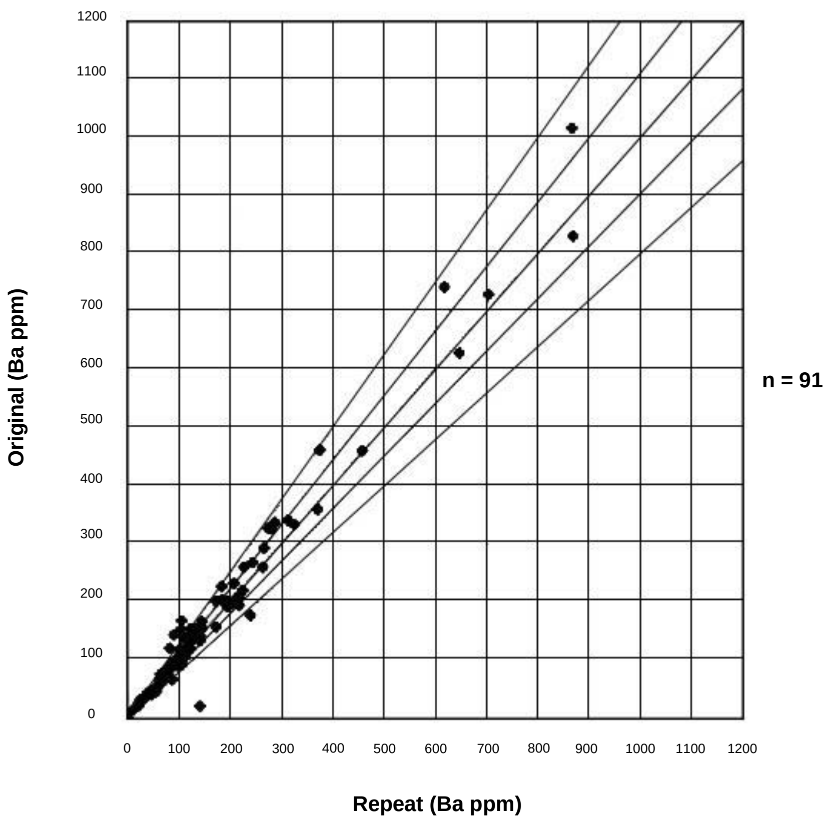


Figure 14. Barium original vs repeat analyses

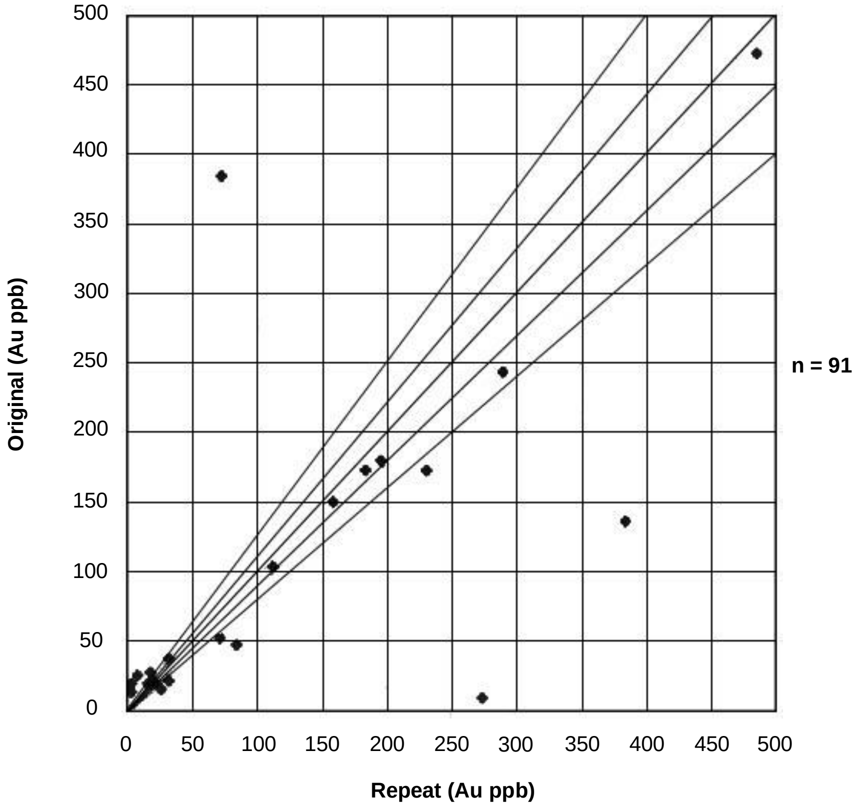


Figure 15. Gold original vs repeat analyses

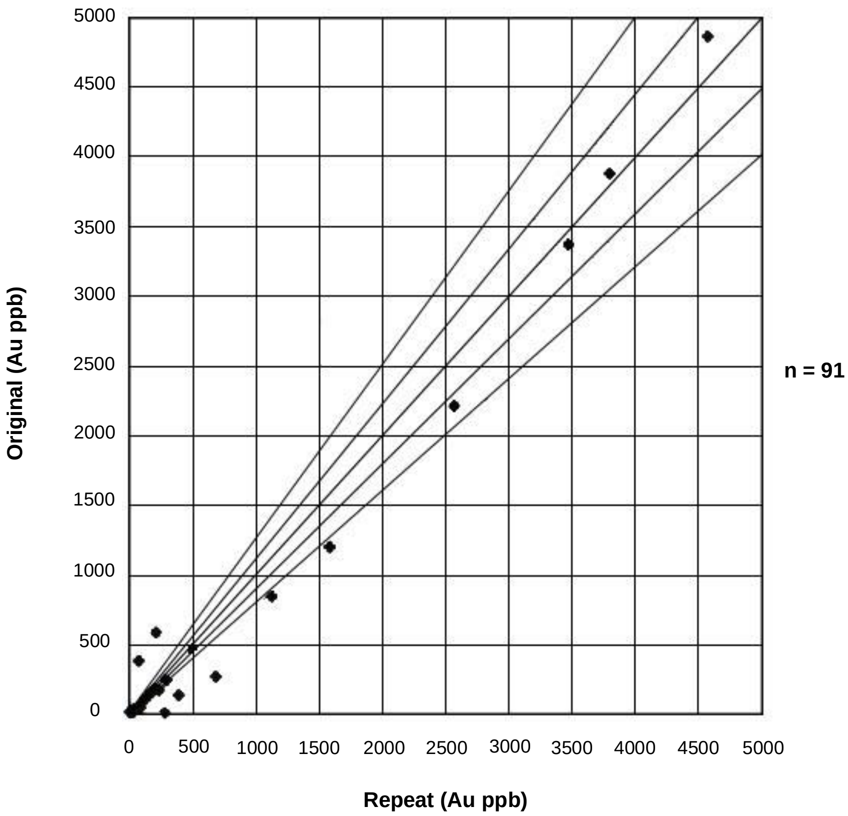


Figure 16. Gold original vs repeat analyses

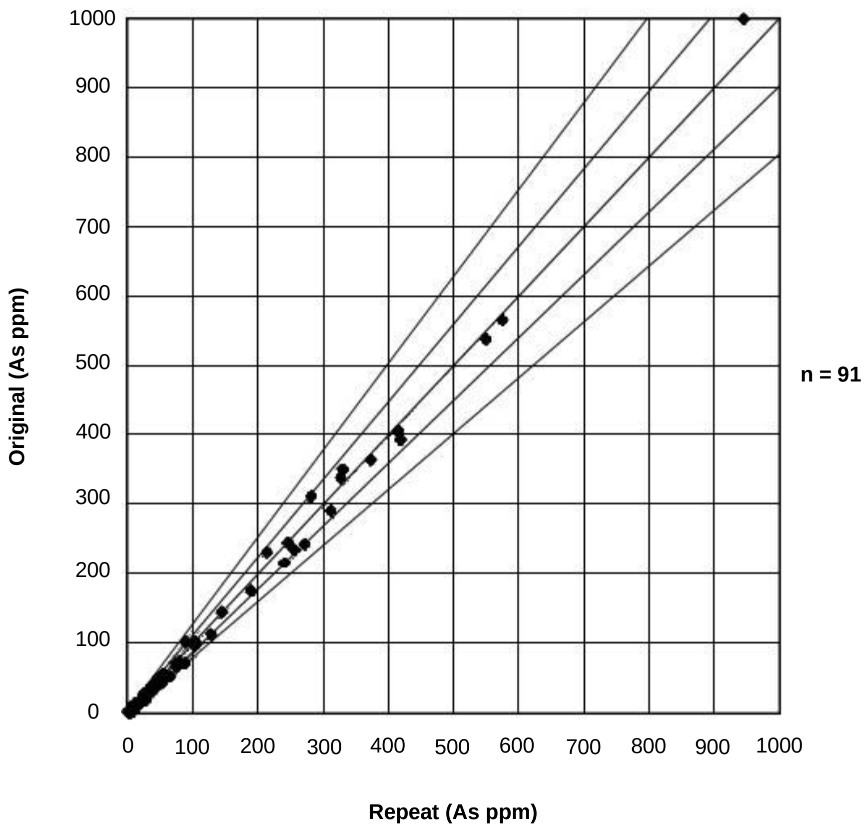


Figure 17. Arsenic original vs repeat analyses

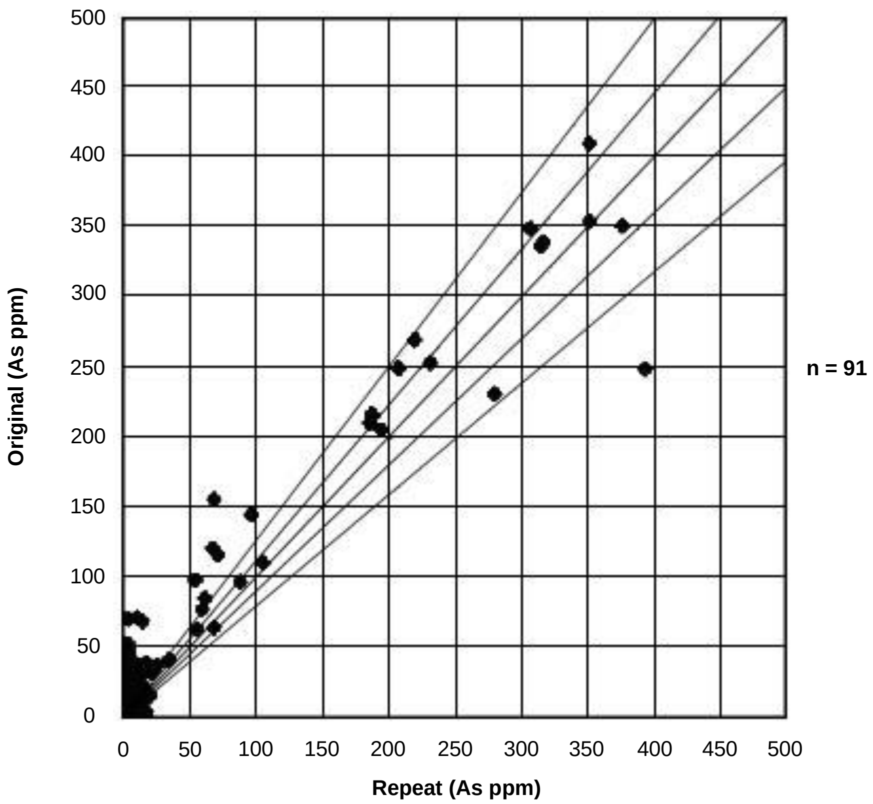


Figure 18. Arsenic original vs repeat analyses (ICP)

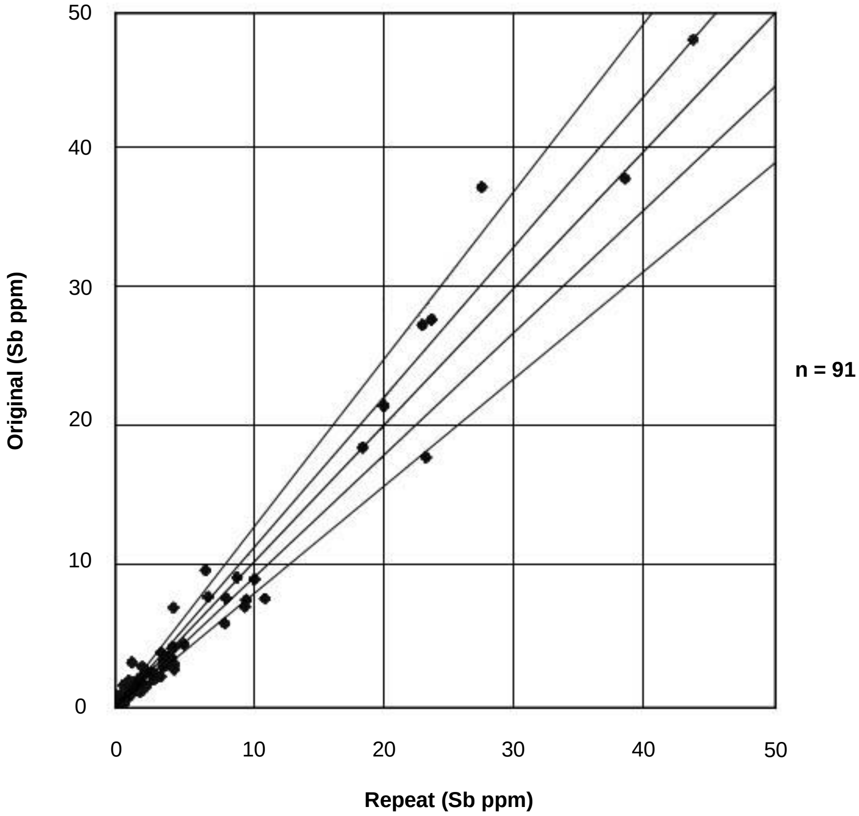


Figure 19. Antimony original vs repeat analyses

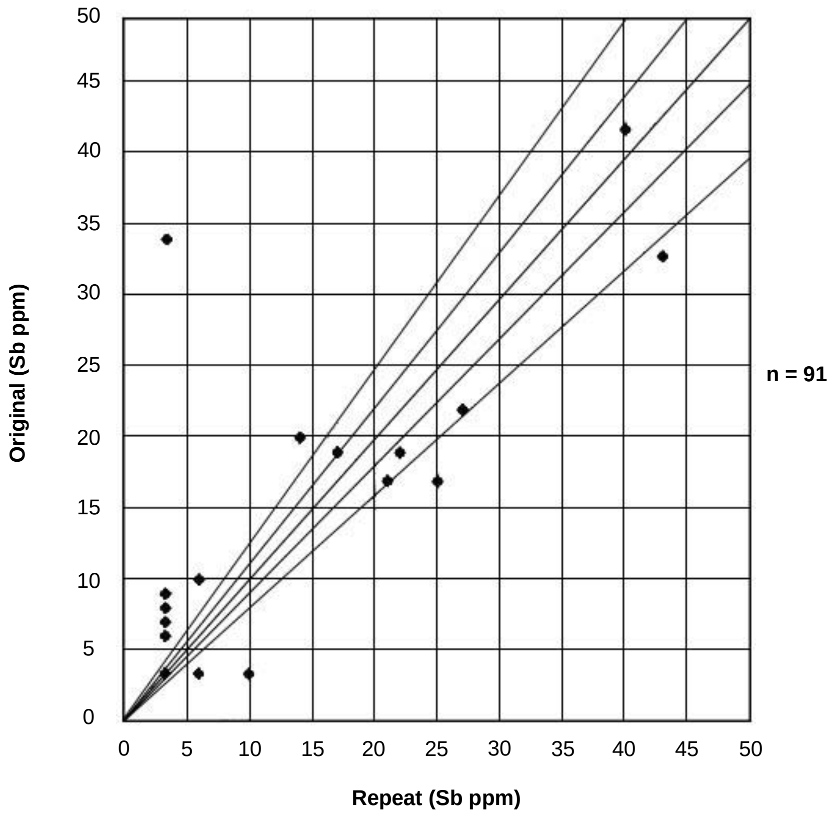


Figure 20. Antimony original vs repeat analyses (ICP)

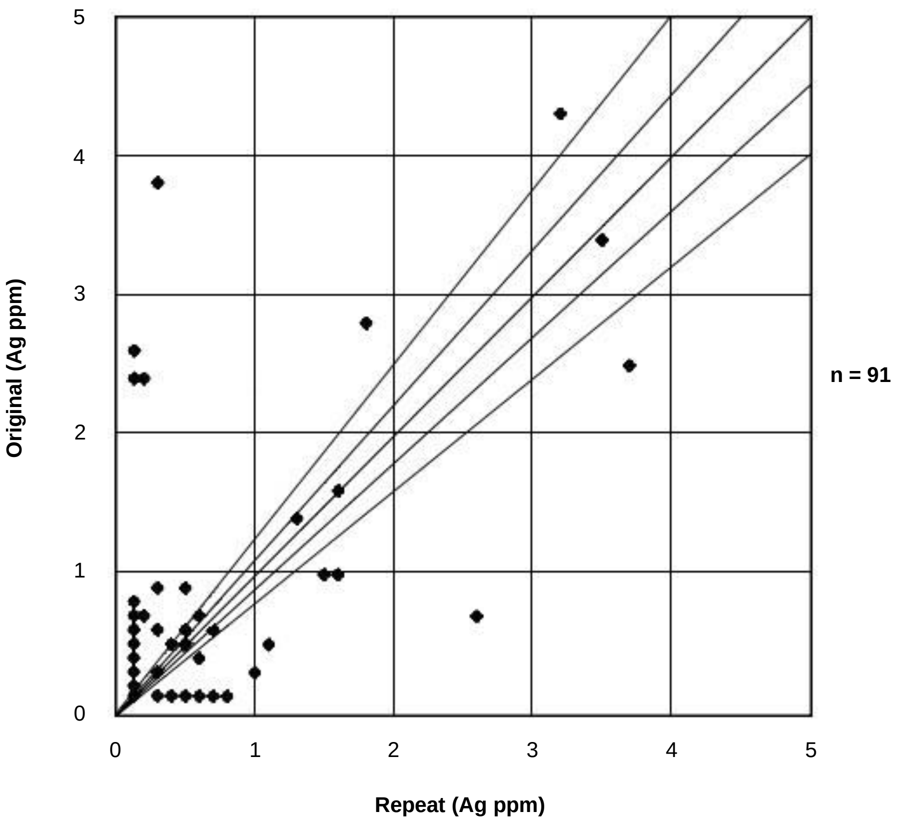


Figure 21. Silver original vs repeat analyses

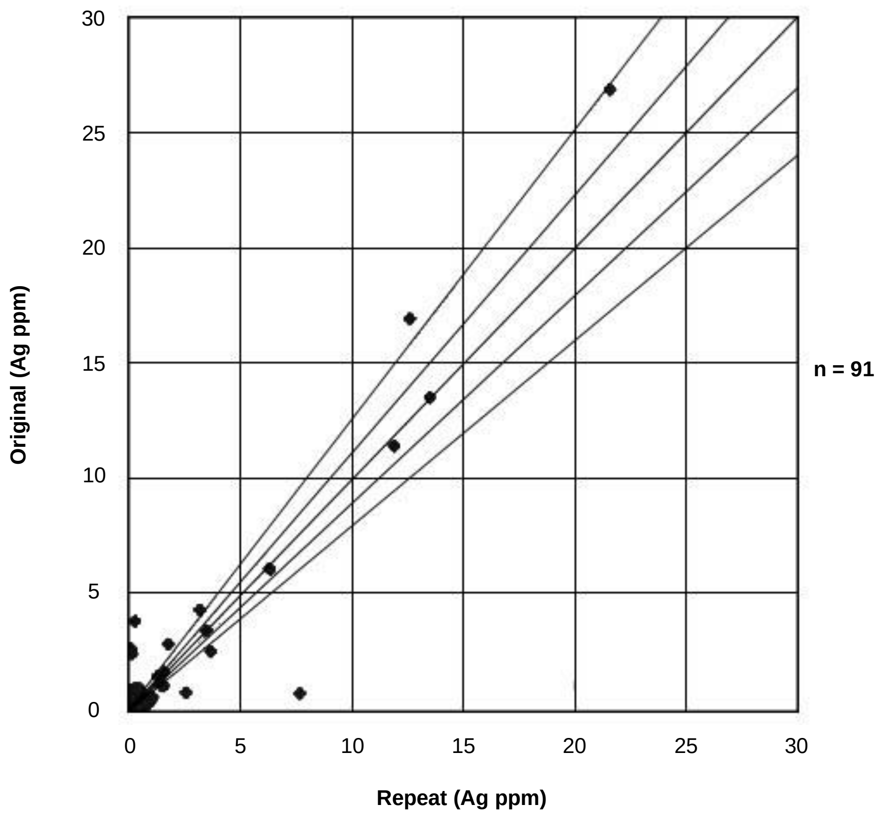


Figure 22. Silver original vs repeat analyses

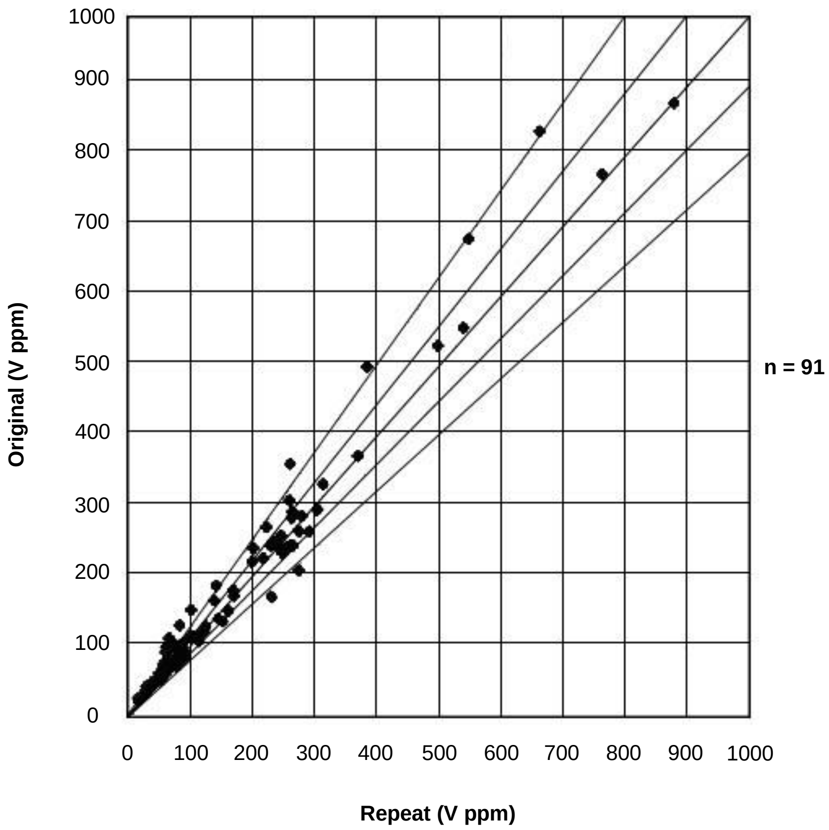


Figure 23. Vanadium original vs repeat analyses

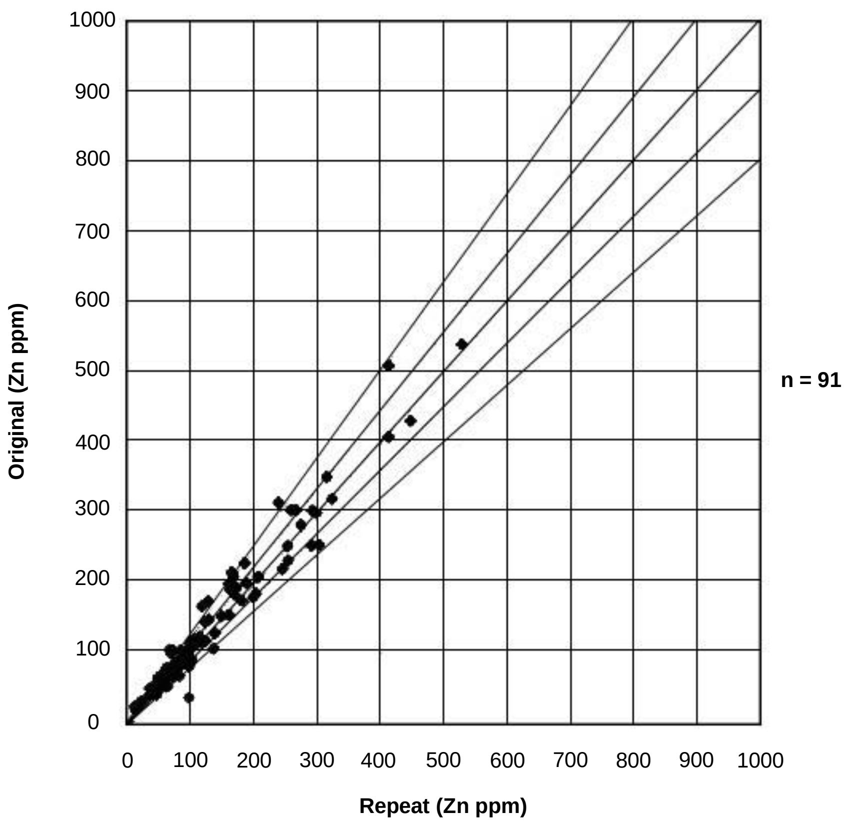


Figure 24. Zinc original vs repeat analyses

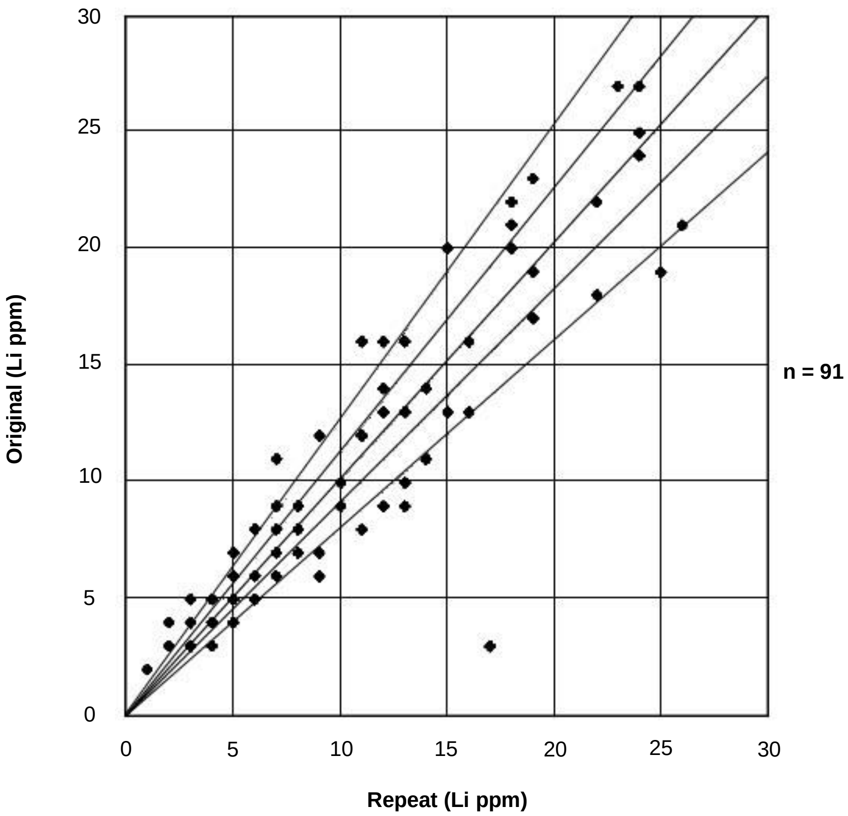
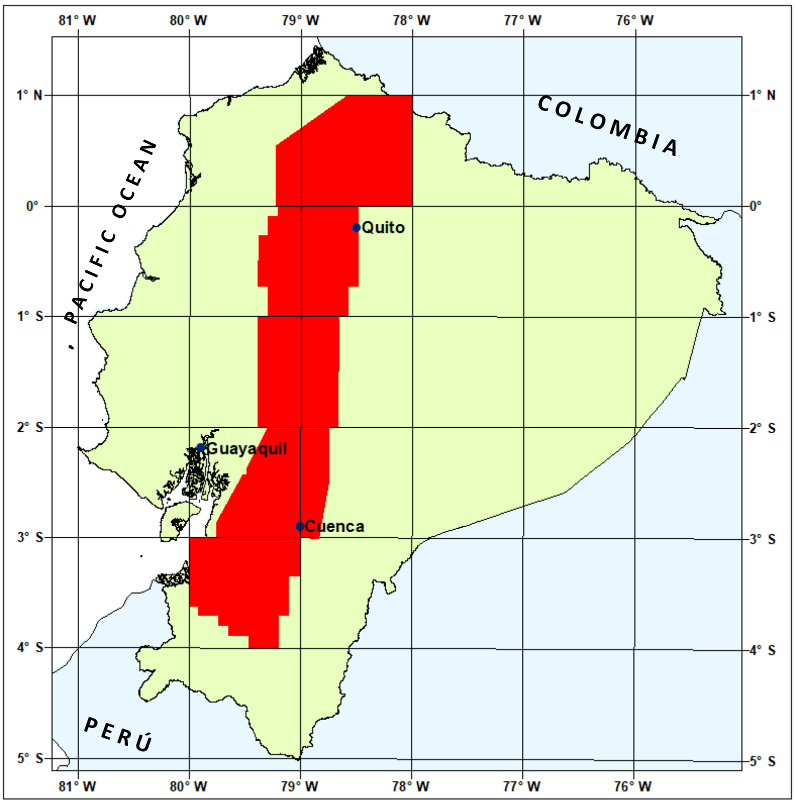


Figure 25. Lithium original vs repeat analyses

APPENDIX 4 OF REPORT:

CONTROL OF QUALITY OF GEOCHEMICAL DATA

THOMPSON AND HOWARTH (1978) PRECISION CONTROL CHARTS



GEOLOGICAL INFORMATION MAPPING PROGRAMME

QUITO, 1997

Thompson and Howarth precision control charts

Analyses from the first year.

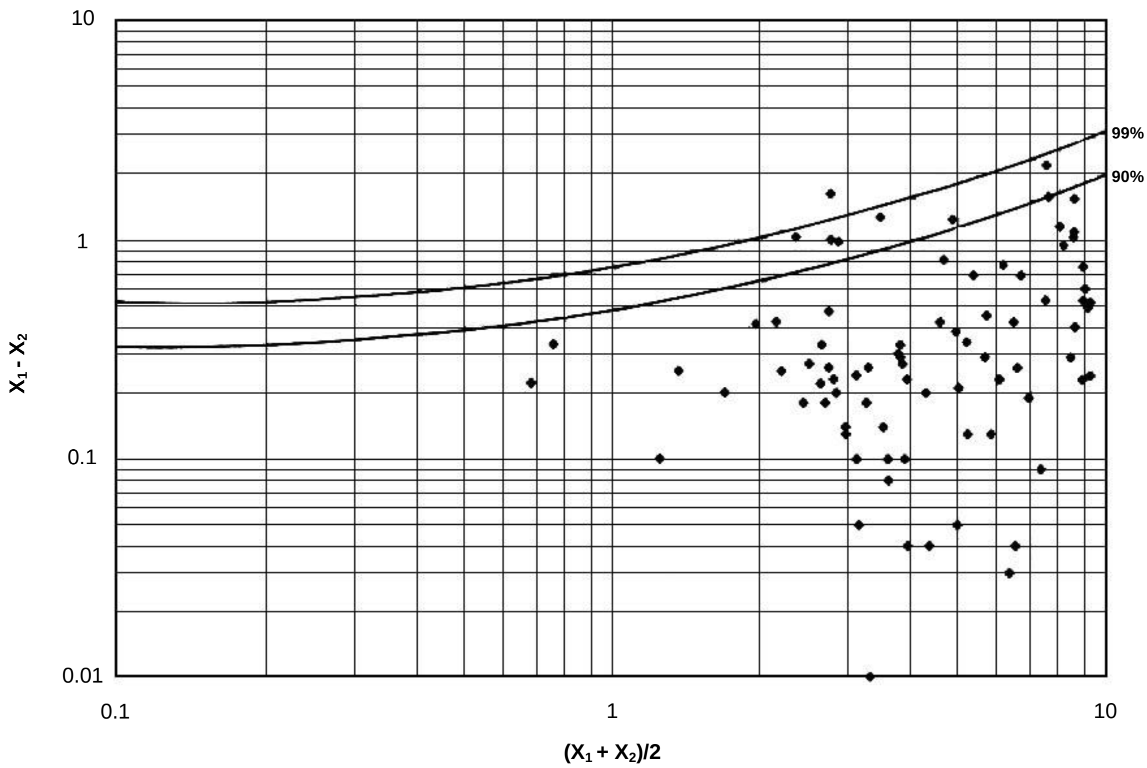


Figure 1. Iron duplicate analyses. Precision = 15%, DL = 0.3%

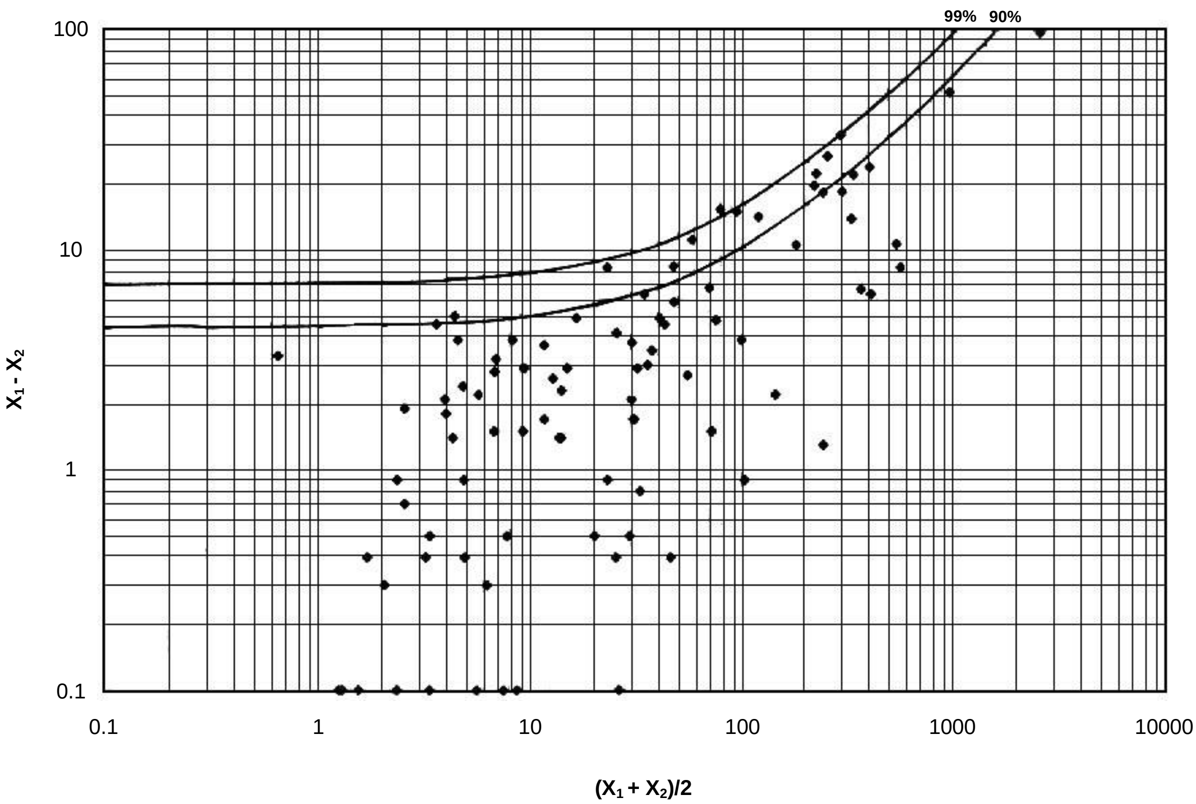


Figure 2. Arsenic duplicate analyses. Precision = 5%, DL = 4 ppm

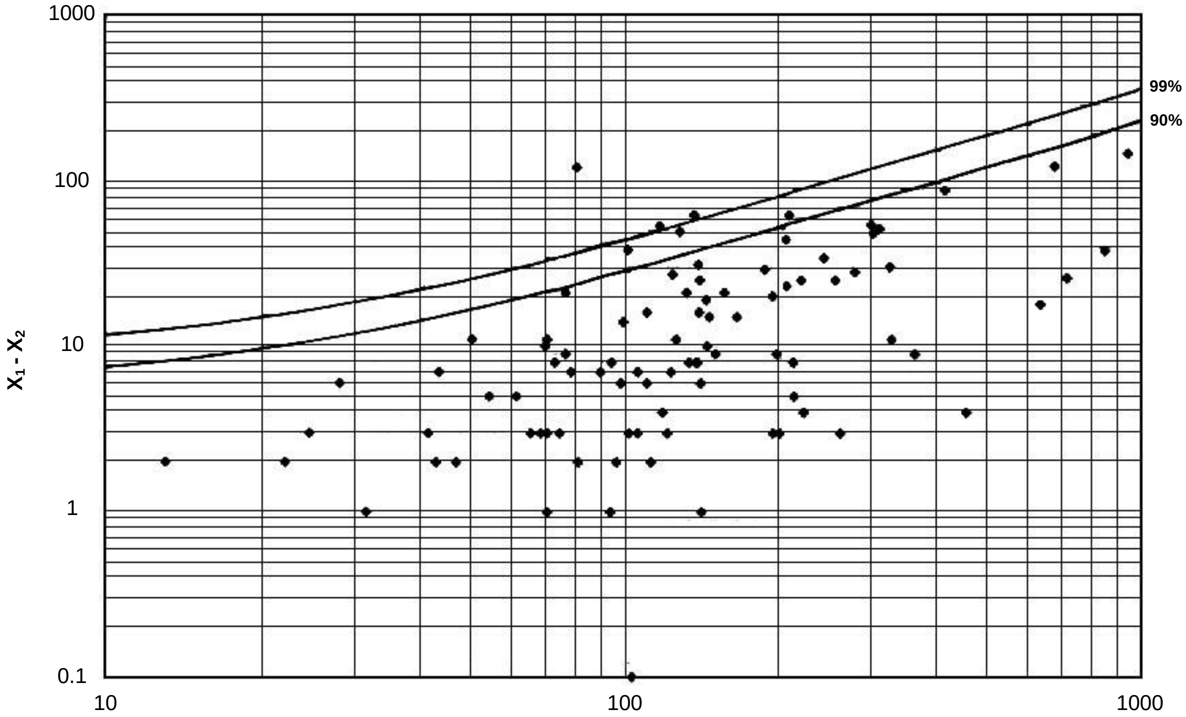


Figure 3. Barium duplicate analyses. Precision = 20%, DL = 5.4 ppm

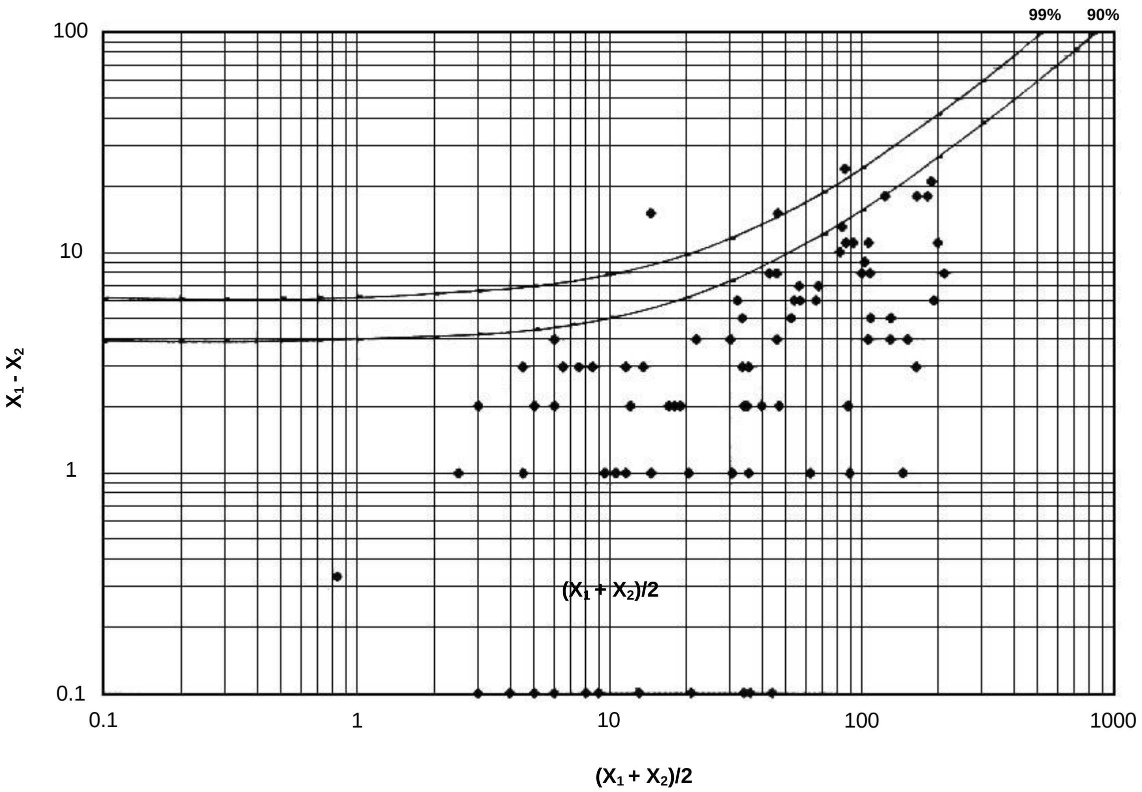


Figure 4. Chromium duplicate analyses. Precision = 10%, DL = 3.7 ppm

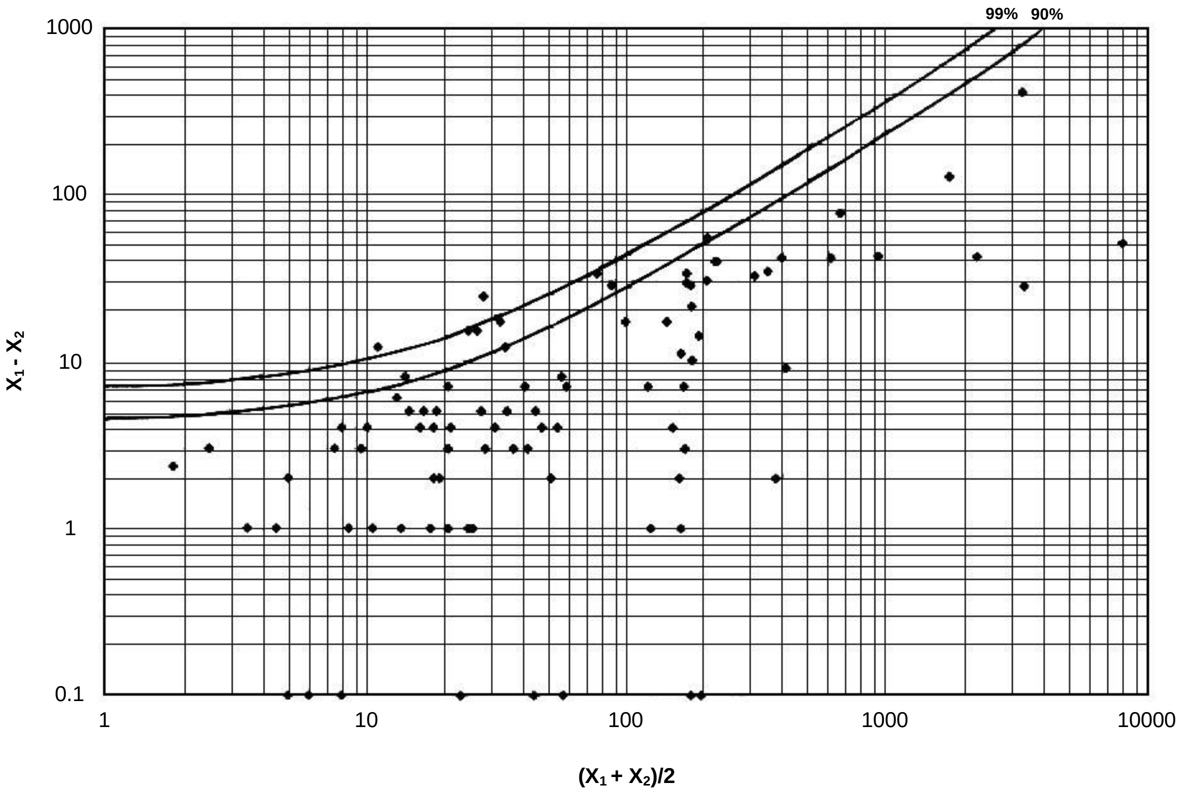


Figure 5. Copper duplicate analyses. Precision = 20%, DL = 4.5 ppm

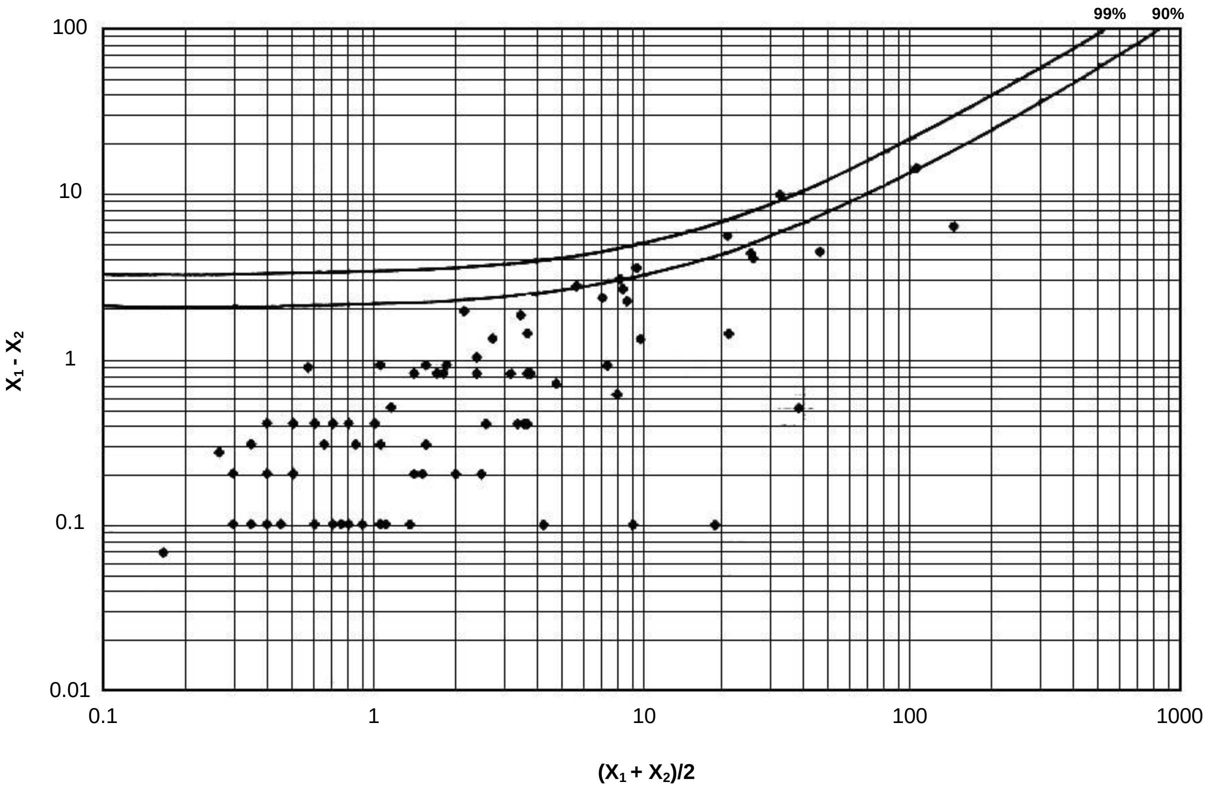


Figure 6. Antimony duplicate analyses. Precision = 10%, DL = 1.9 ppm

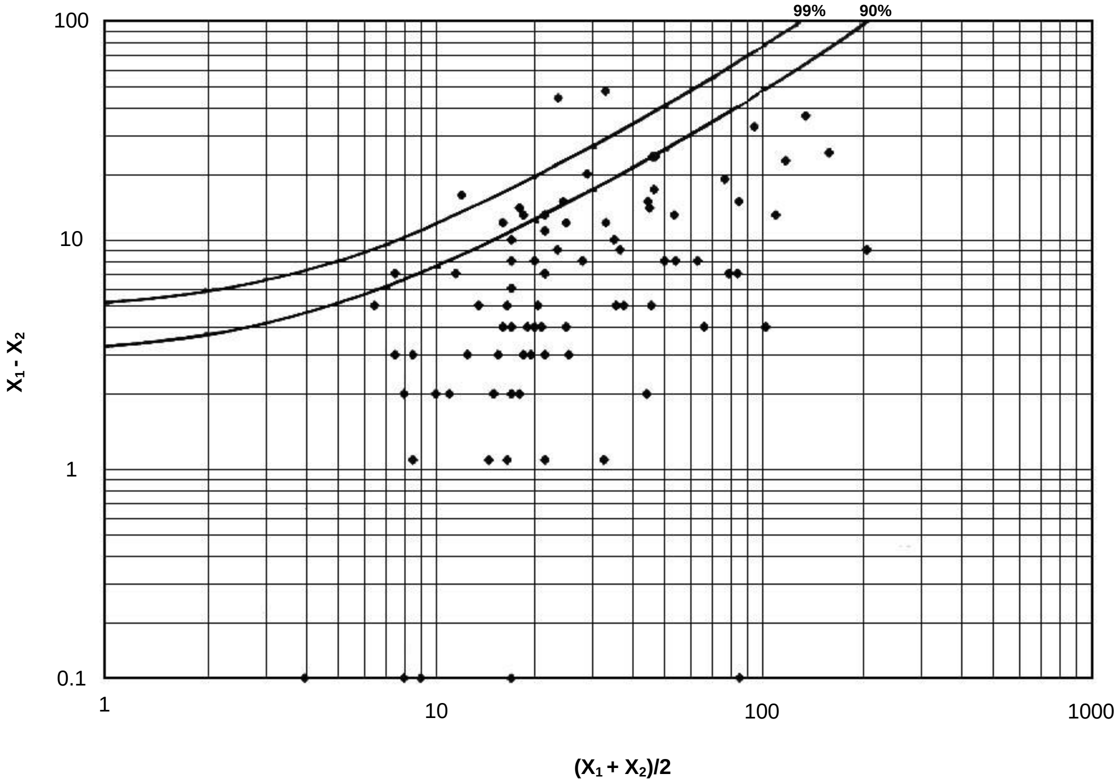


Figure 7. Lead duplicate analyses. Precision = 40%, DL = 4 ppm

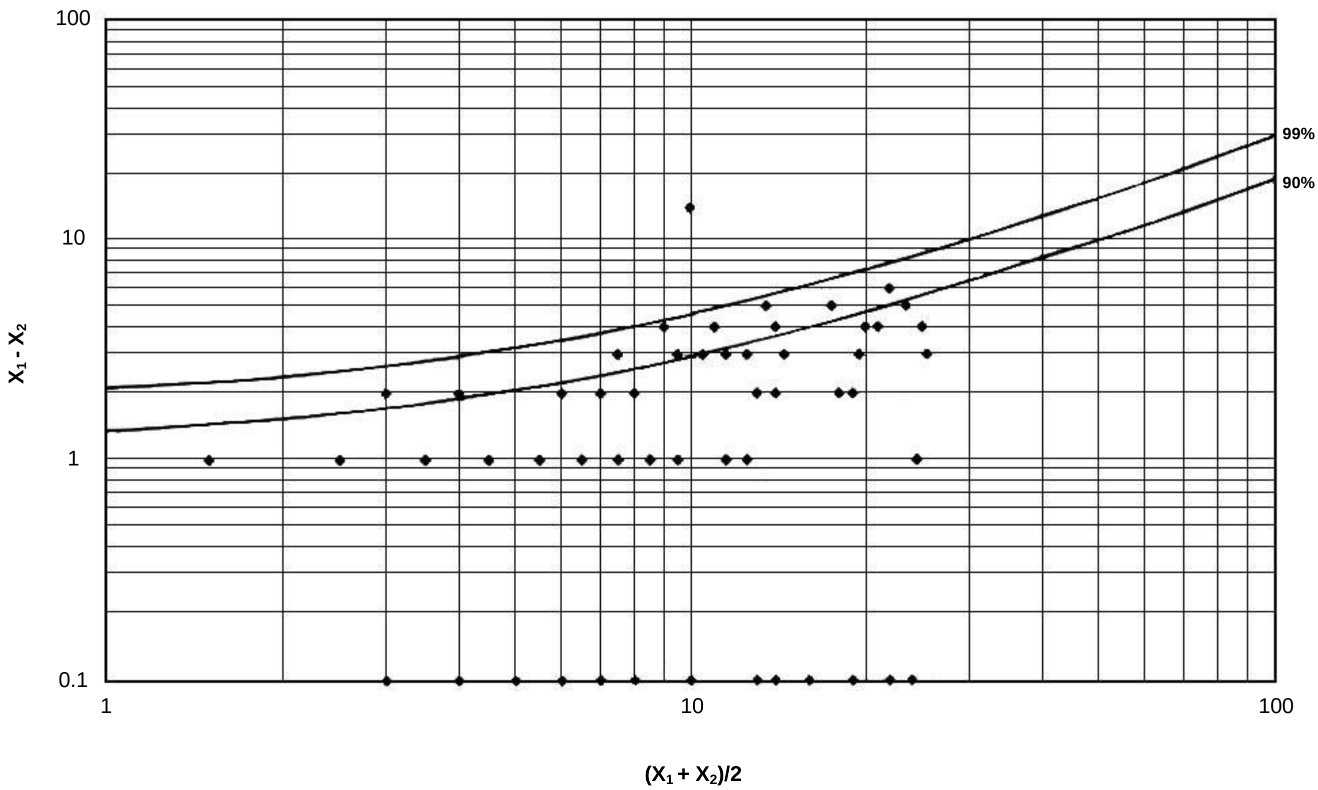


Figure 8. Lithium duplicate analyses. Precision = 15%, DL = 1.2 ppm

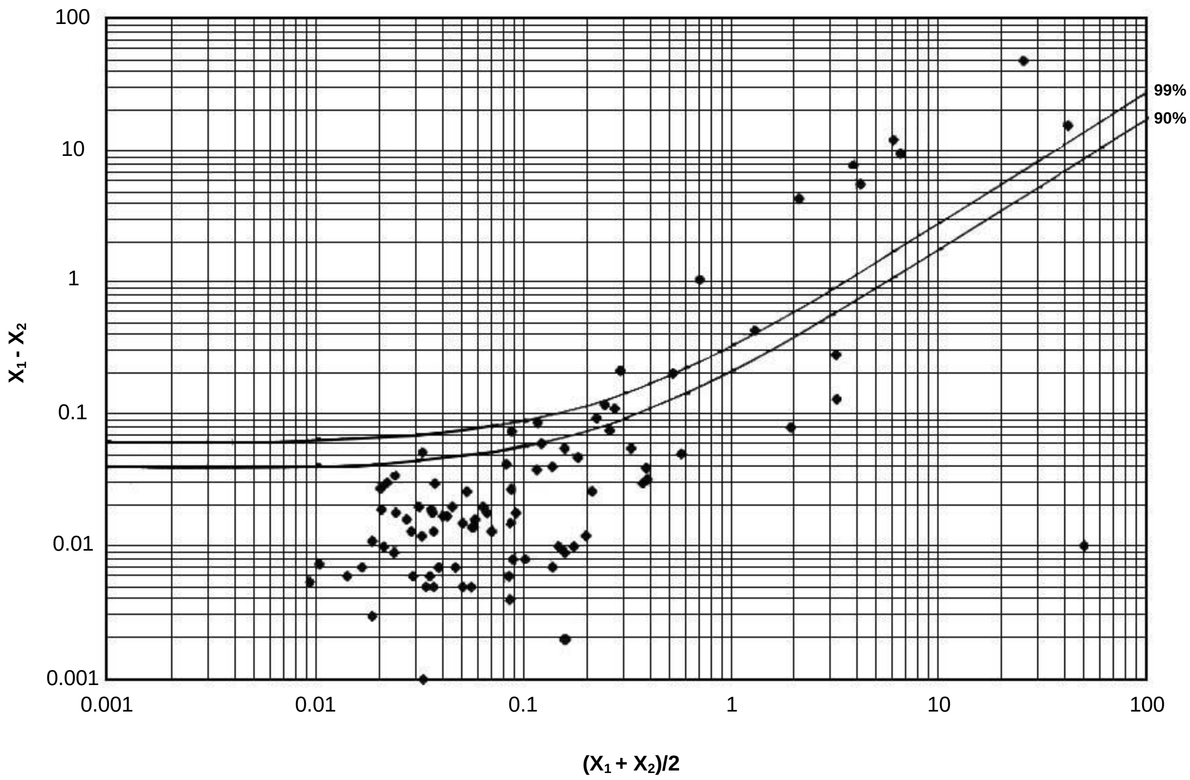


Figure 9. Mercury duplicate analyses. Precision = 15%, DL = 0.04 ppm

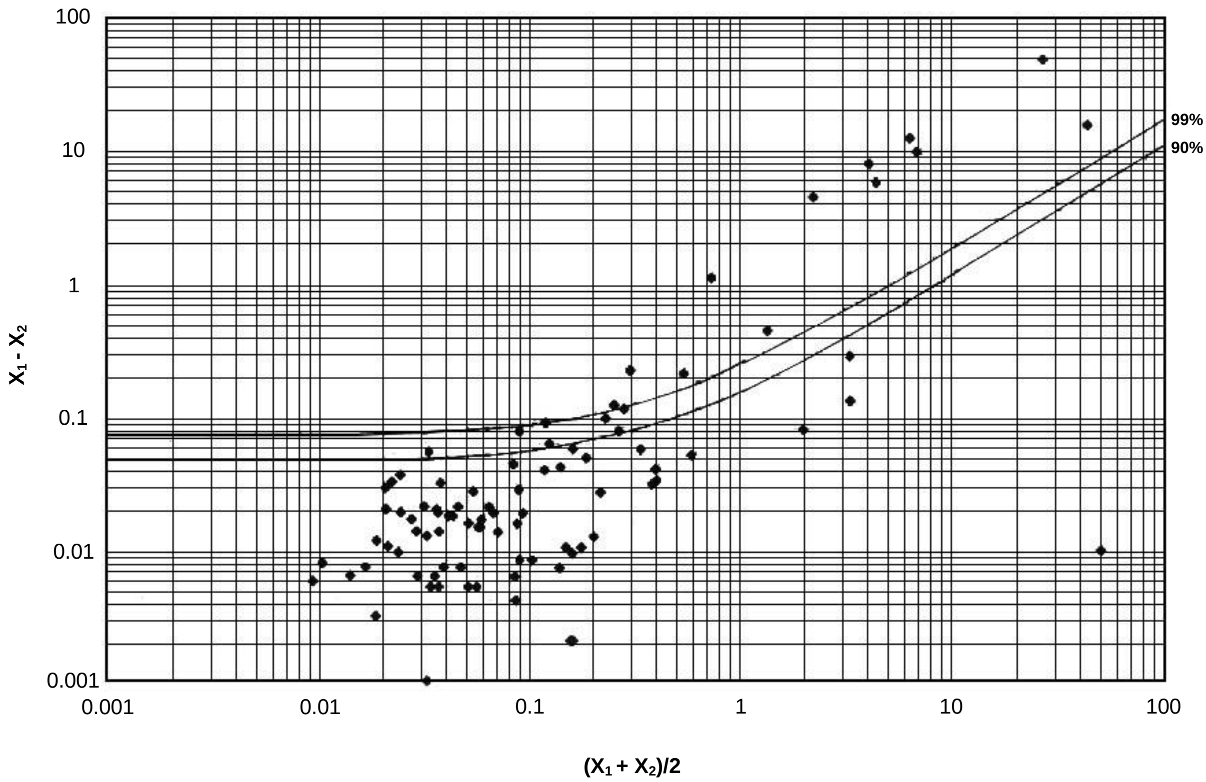


Figure 10. Mercury duplicate analyses. Precision = 10%, DL = 0.04 ppm

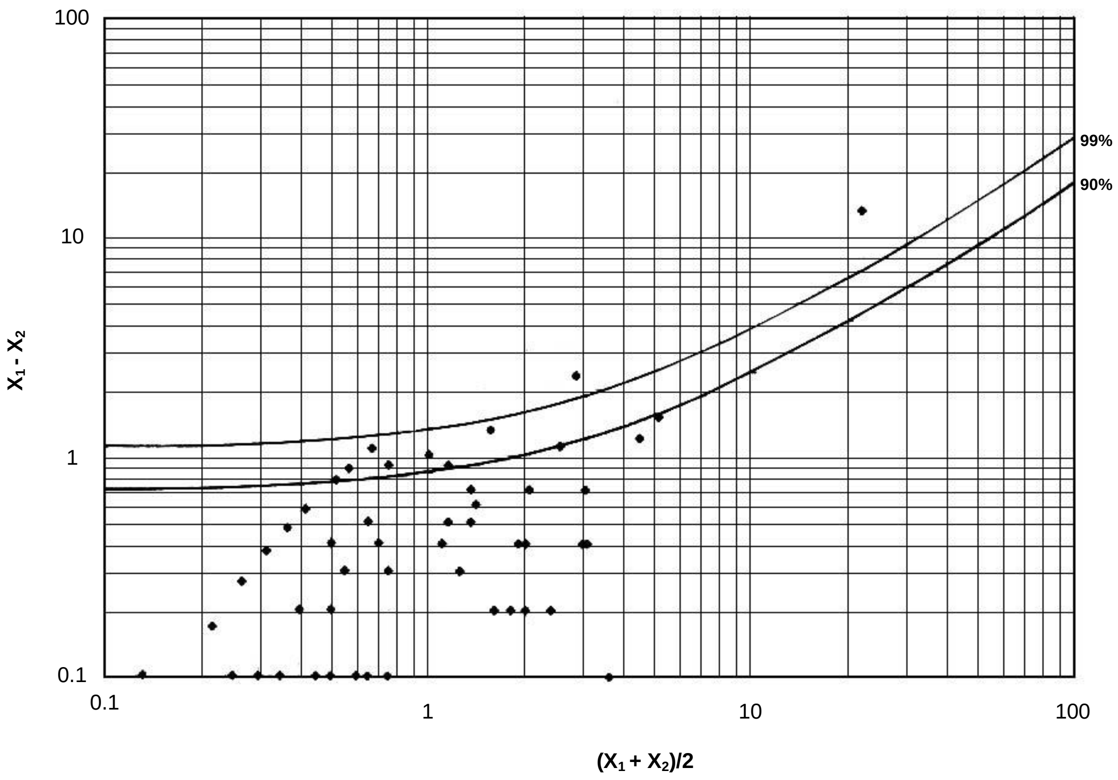


Figure 11. Cadmium duplicate analyses. Precision = 15%, DL = 0.67 ppm

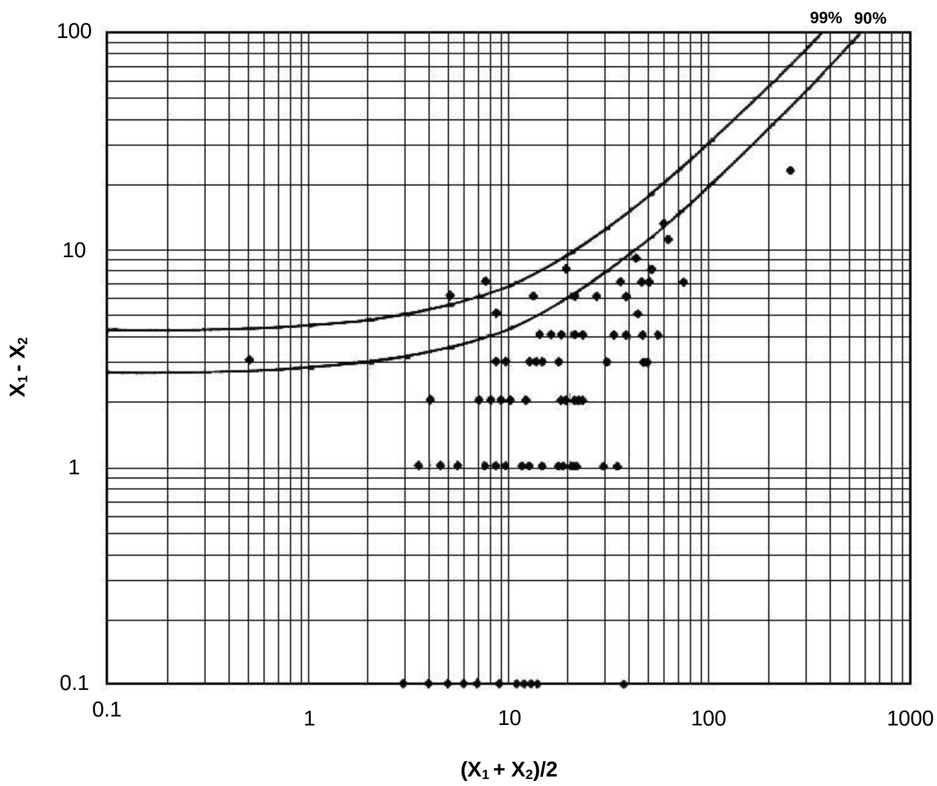


Figure 12. Cobalt duplicate analyses. Precision = 15%, DL = 2.6 ppm

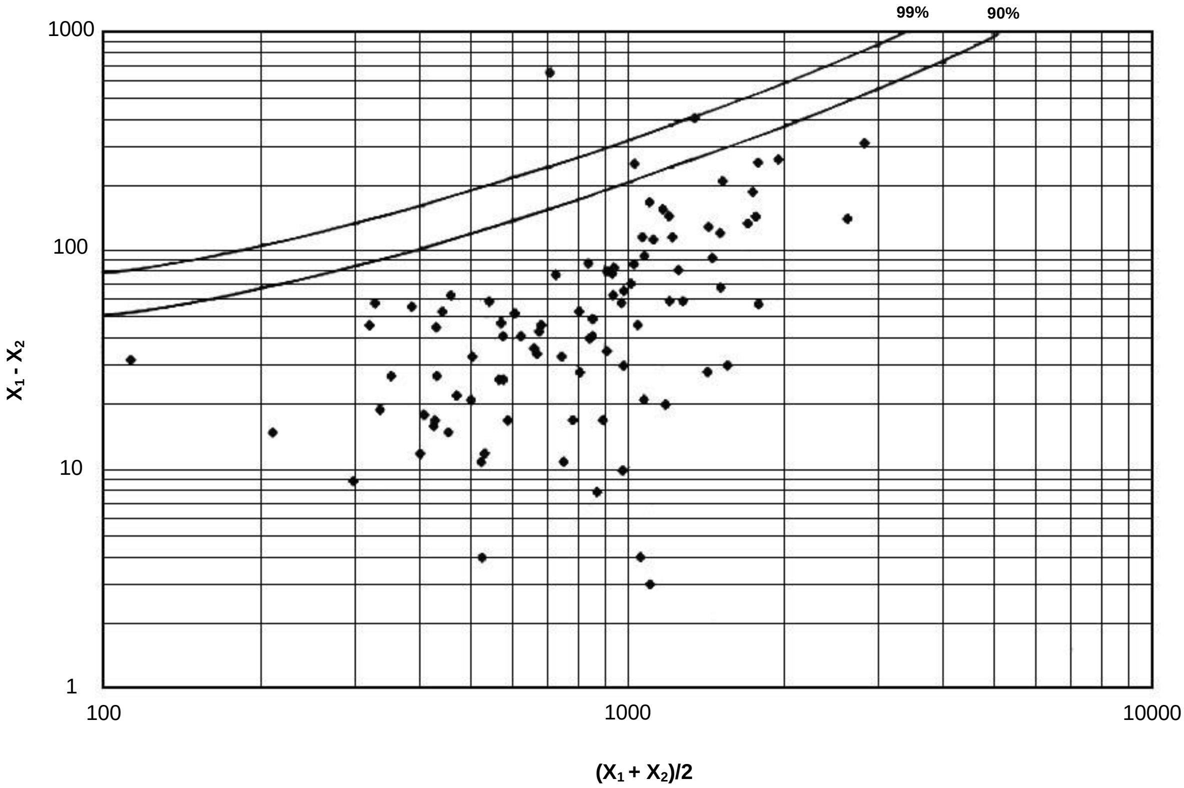


Figure 13. Manganese duplicate analyses. Precision = 15%, DL = 34 ppm

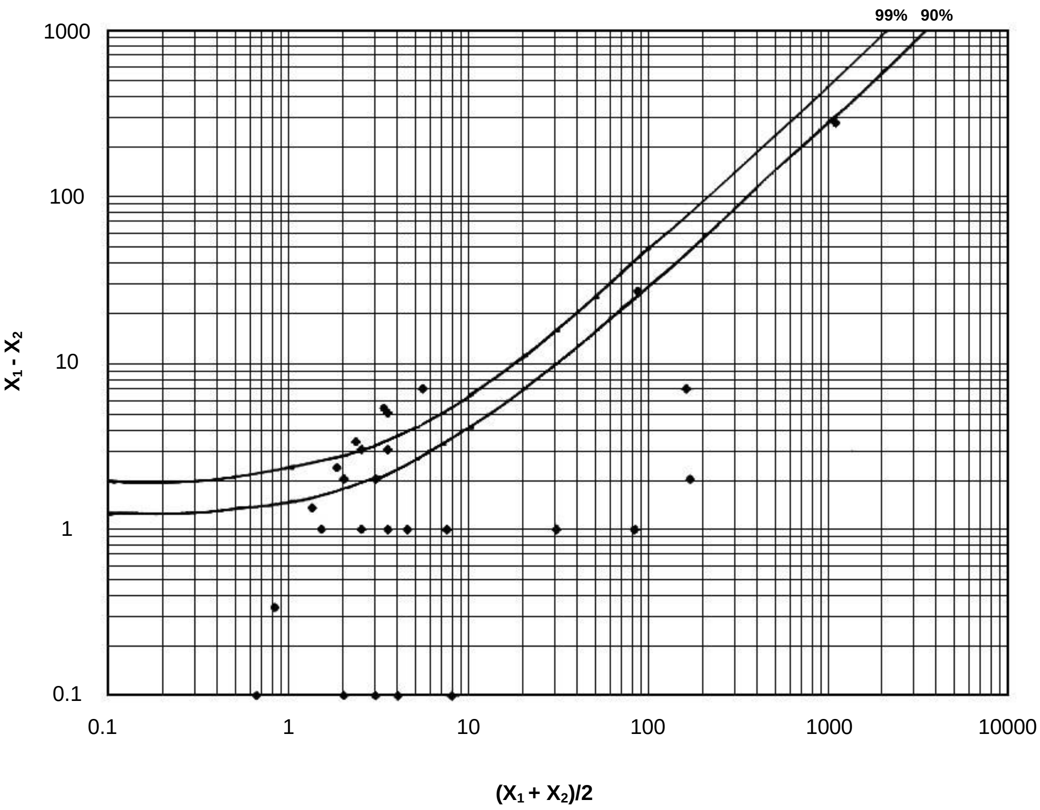


Figure 14. Molybdenum duplicate analyses. Precision = 25%, DL = 1.35 ppm

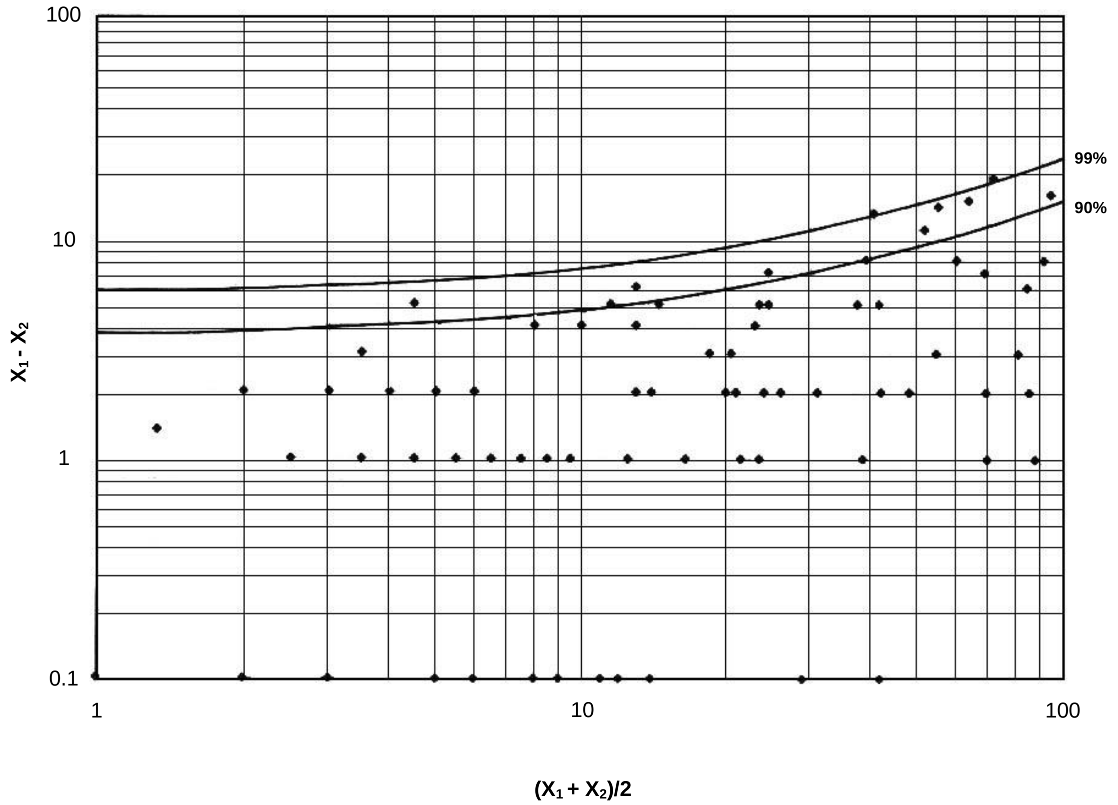


Figure 15. Nickel duplicate analyses. Precision = 10%, DL = 3.3 ppm

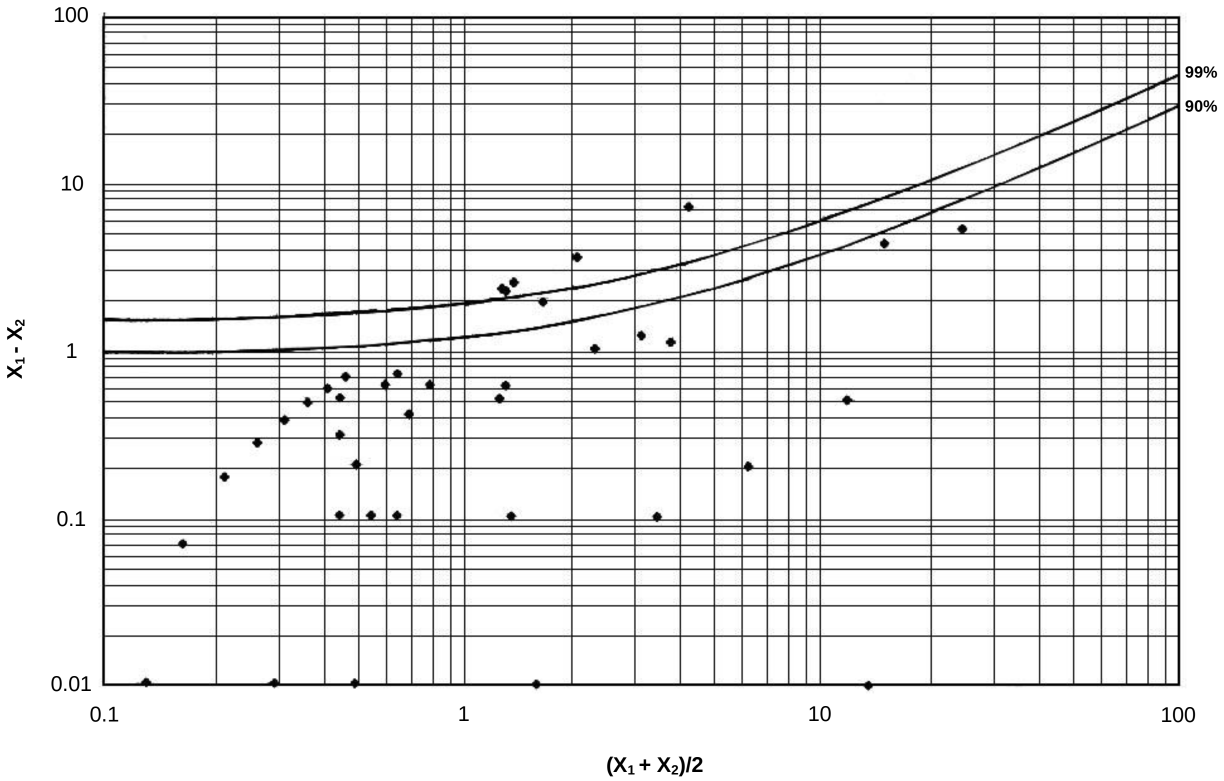


Figure 16. Silver duplicate analyses. Precision = 25%, DL = 1 ppm

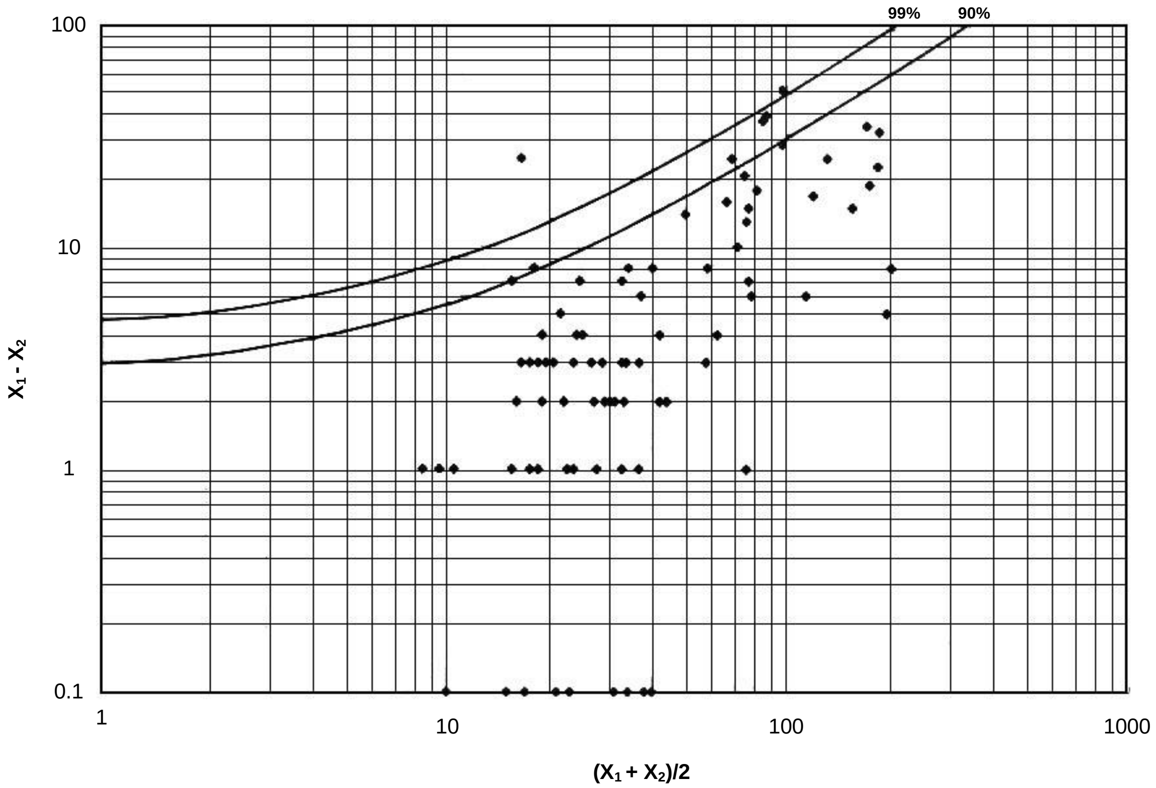


Figure 17. Strontium duplicate analyses. Precision = 25%, DL = 3 ppm

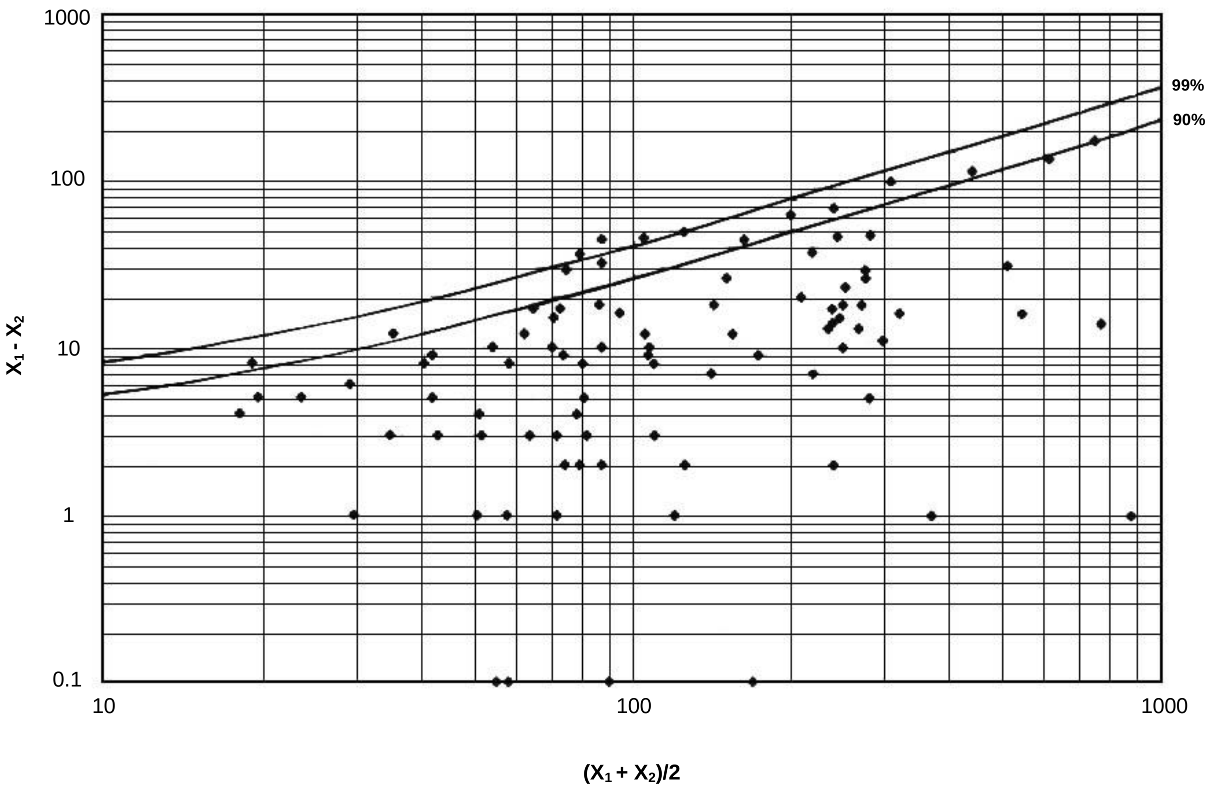


Figure 18. Vanadium duplicate analyses. Precision = 20%, DL = 3 ppm

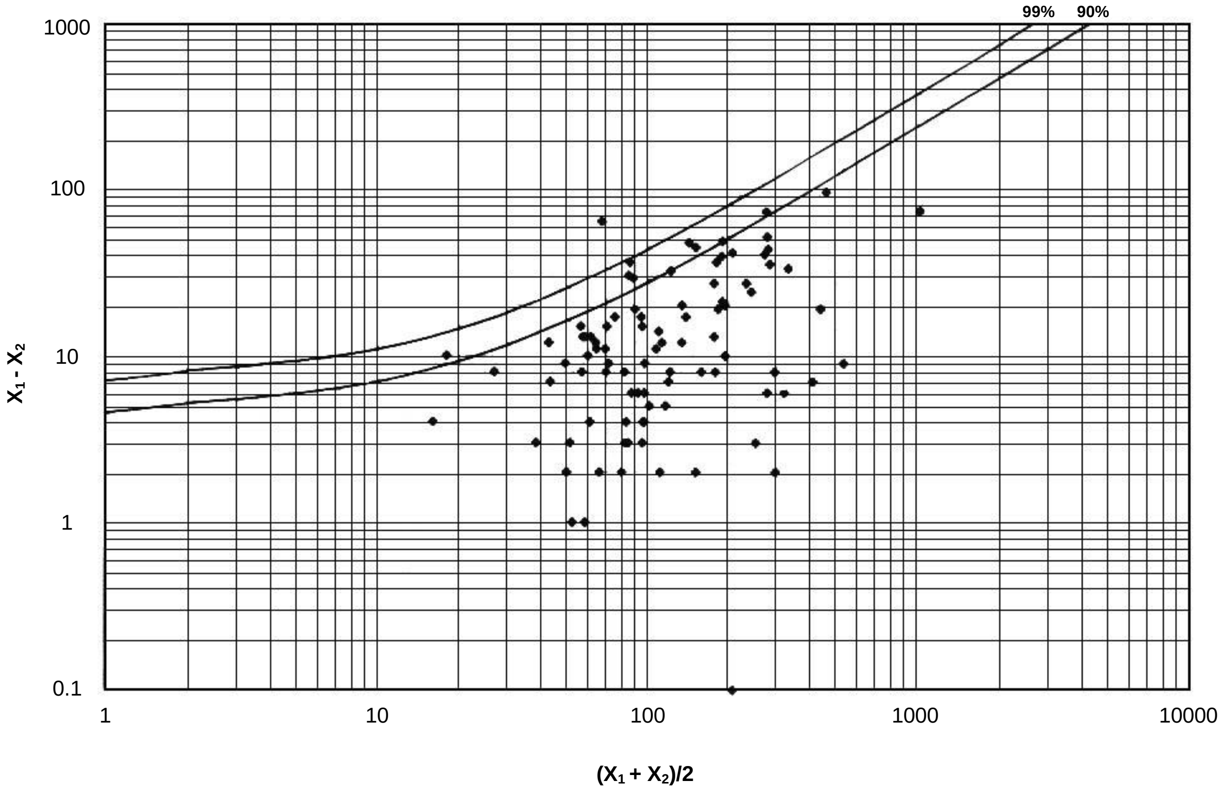
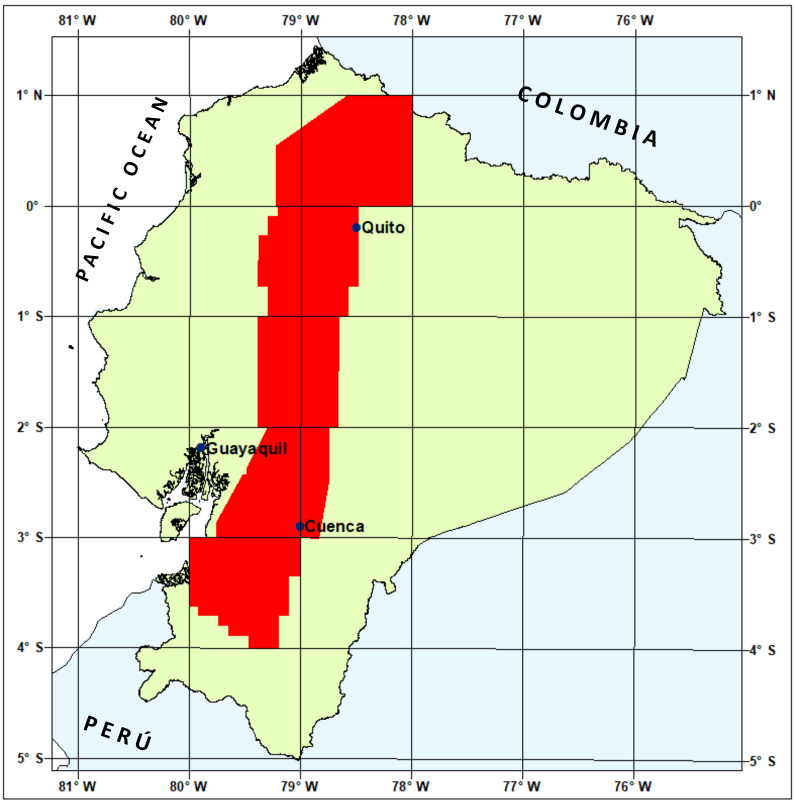


Figure 19. Zinc duplicate analyses. Precision = 20%, DL = 5 ppm

APPENDIX 5 OF REPORT:

CONTROL OF QUALITY OF GEOCHEMICAL DATA

COEFFICIENT OF VARIATION ANALYSIS AND MEAN VS MEDIAN OF DIFFERENCES PLOTS



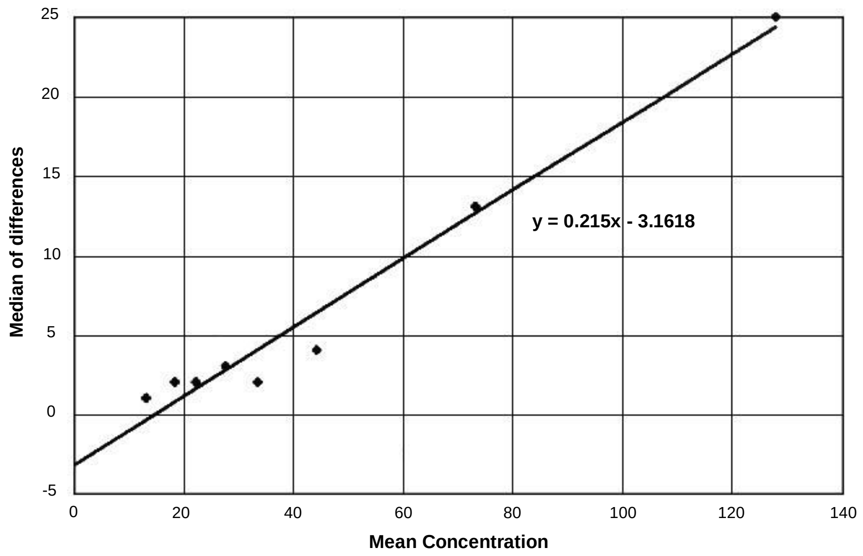
GEOLOGICAL INFORMATION MAPPING PROGRAMME

QUITO, 1997

The following graphs show the median of differences plotted against the mean of means for groups of duplicate analyses, using the method of Thompson and Howarth (1978) (see text, Method 1). Each point represents the median of differences plotted against the mean of means for groups of 11 duplicate analyses arranged in order of increasing concentration. The intercept represents s_0 and the gradient (x) represents k in the equations of Thompson and Howarth.

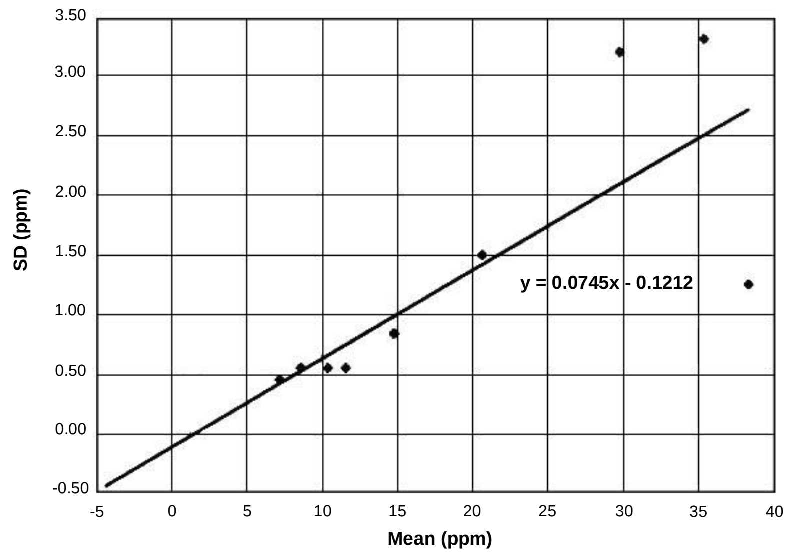
The graphs also show the mean concentration plotted against standard deviation (SD) for replicate analyses of reference samples. Lines fitted by linear regression. The intercept is equivalent to the standard deviation at zero concentration (s_0) and the gradient (x) is equivalent to k in the equations of Thompson and Howarth (1978).

Analyses from the first year.



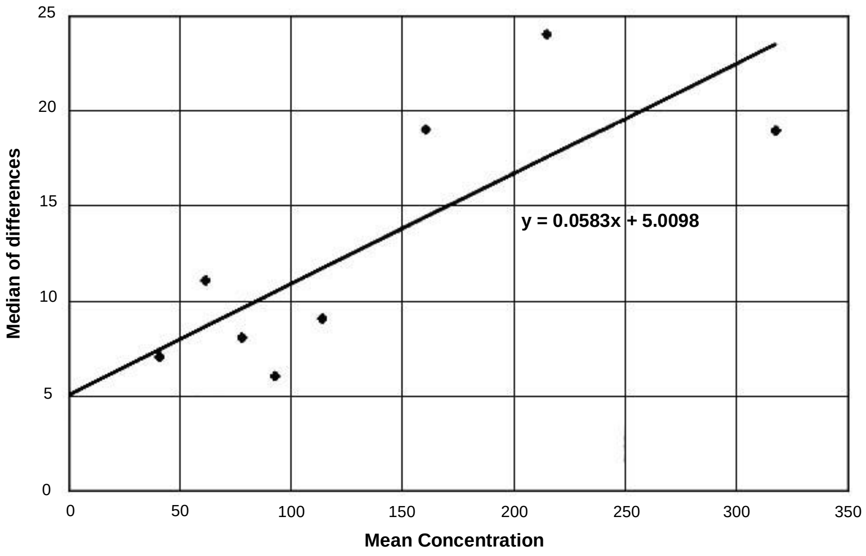
Mean	Median
13.000	1
18.273	2
22.091	2
27.455	3
33.364	2
44.136	4
73.182	13
128.00	25

Figure 1. Strontium. Regression of median of differences on mean of groups of duplicate analyses



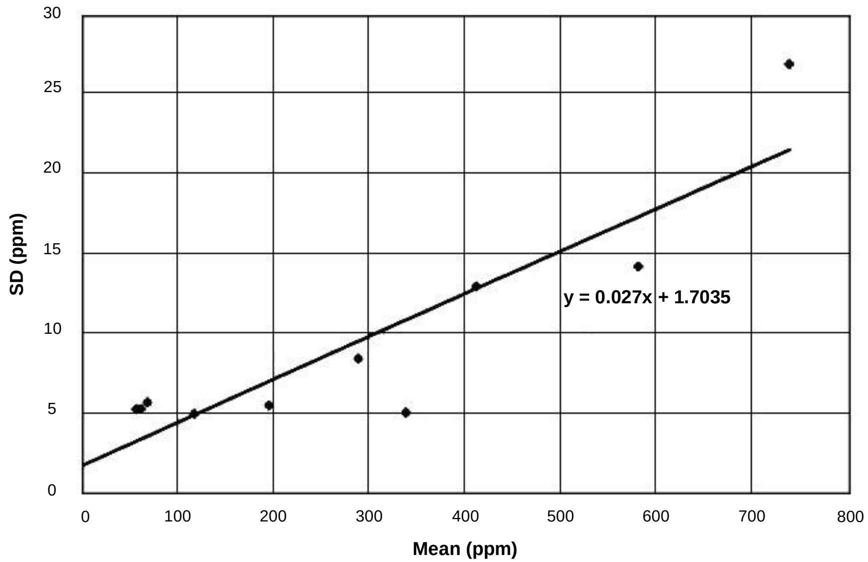
Samples	Mean	SD
STANDARD 1	10.40	0.5477
STANDARD 2	7.20	0.4472
STANDARD 3	8.60	0.5477
STANDARD 4	14.80	0.8367
STANDARD 5	11.60	0.5477
STANDARD 6	38.25	1.2583
STANDARD 7	14.80	0.8367
J-1	20.64	1.4960
COR-1	35.36	3.3246
M-1	29.79	3.2129

Figure 2. Strontium. Regression of standard deviation on mean of replicate analyses of standard samples



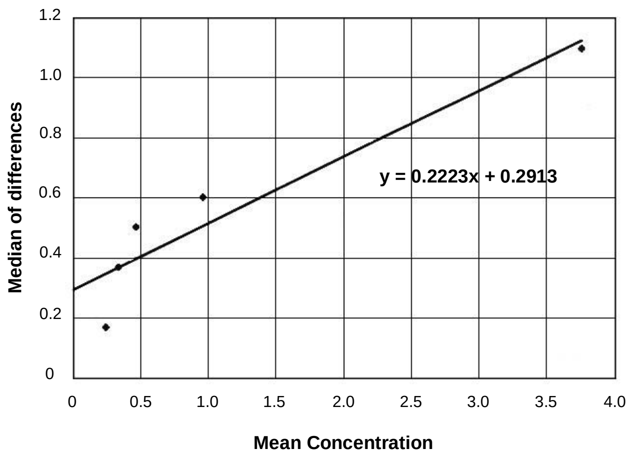
Mean	Median
40.55	7
61.45	11
77.64	8
92.59	6
113.95	9
160.77	19
215.50	24
317.73	19

Figure 3. Zinc. Regression of median of differences on mean of groups of duplicate analyses



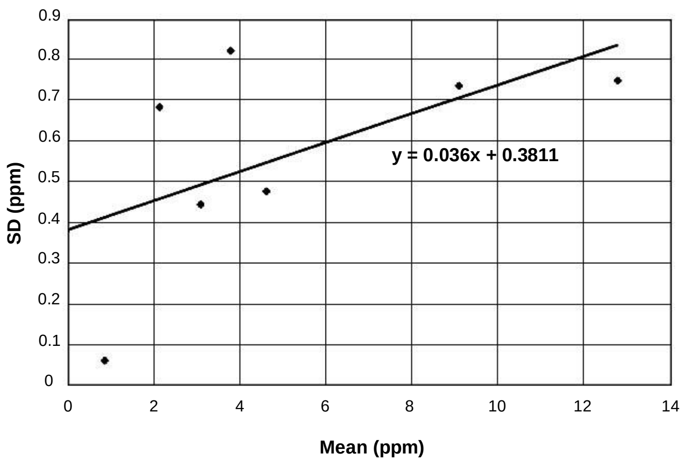
Samples	Mean	SD
STANDARD 1	412.40	12.9731
STANDARD 2	738.60	27.0426
STANDARD 3	580.60	14.2934
STANDARD 4	195.00	5.4772
STANDARD 5	339.00	5.0498
STANDARD 6	116.50	4.9329
STANDARD 7	288.80	8.4083
J-1	67.71	5.6362
COR-1	55.93	5.2134
M-1	60.86	5.2190

Figure 4. Zinc. Regression of standard deviation on mean of replicate analyses of standard samples



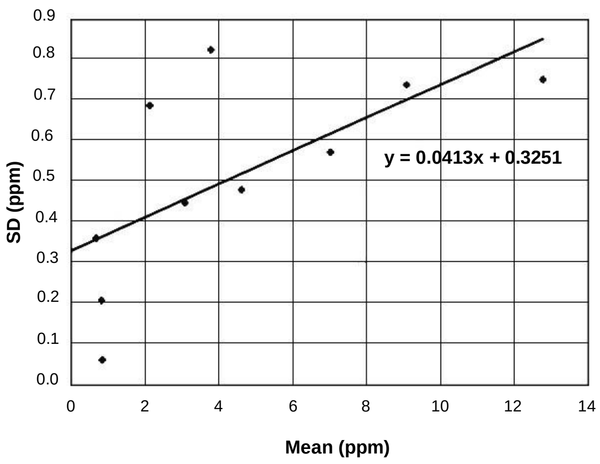
Mean	Median
0.239	0.167
0.333	0.367
0.462	0.500
0.956	0.600
3.756	1.100

Figure 5. Silver. Regression of median of differences on mean of groups of duplicate analyses



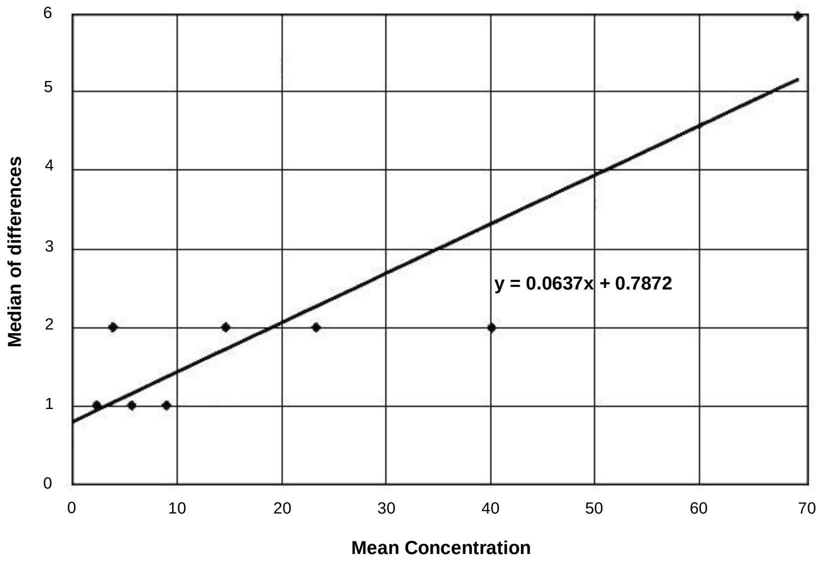
Samples	Mean	SD
STANDARD 1	3.78	0.8228
STANDARD 2	12.78	0.7530
STANDARD 3	9.10	0.7382
STANDARD 4	2.12	0.6834
STANDARD 5	3.08	0.4438
STANDARD 6	0.85	0.0577
STANDARD 7	4.62	0.4764

Figure 6. Silver. Regression of standard deviation on mean of replicate analyses of standard samples



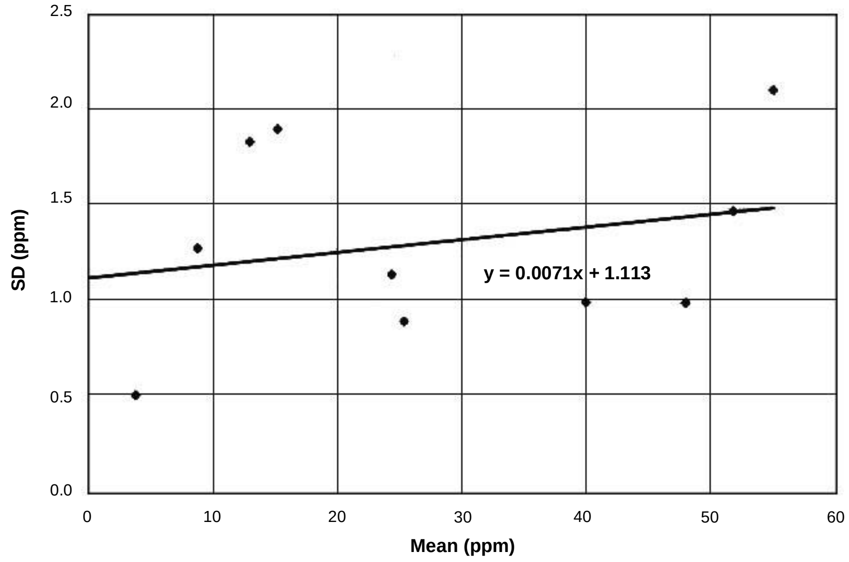
Samples	Mean	SD
STANDARD 1	3.78	0.8228
STANDARD 2	12.78	0.7530
STANDARD 3	9.10	0.7382
STANDARD 4	2.12	0.6834
STANDARD 5	3.08	0.4438
STANDARD 6	0.85	0.0577
STANDARD 7	4.62	0.4764
BCC3	7.04	0.56999
BCC4	0.82	0.204396
BCC5	0.672167	0.355947

Figure 7. Silver. Regression of standard deviation on mean of replicate analyses of standard samples



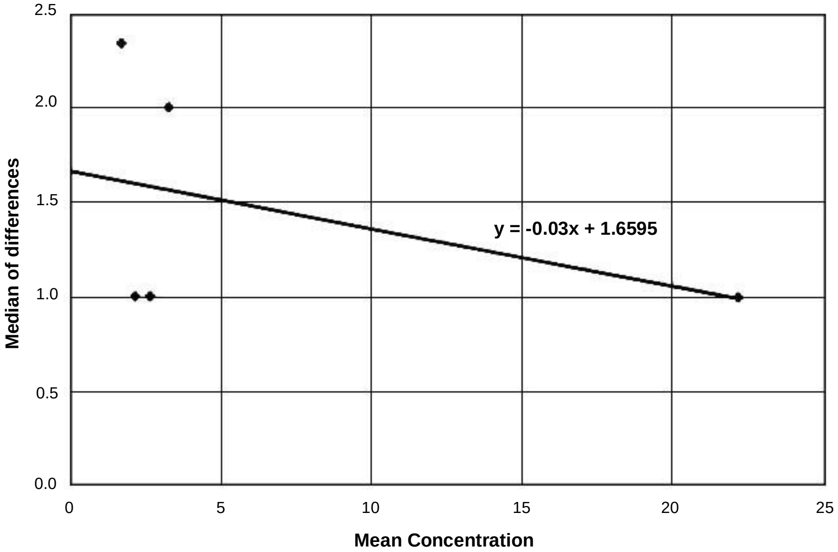
Mean	Median
2.348	1
3.909	2
5.682	1
9.000	1
14.636	2
23.273	2
40.045	2
69.182	6

Figure 8. Nickel. Regression of median of differences on mean of groups of duplicate analyses



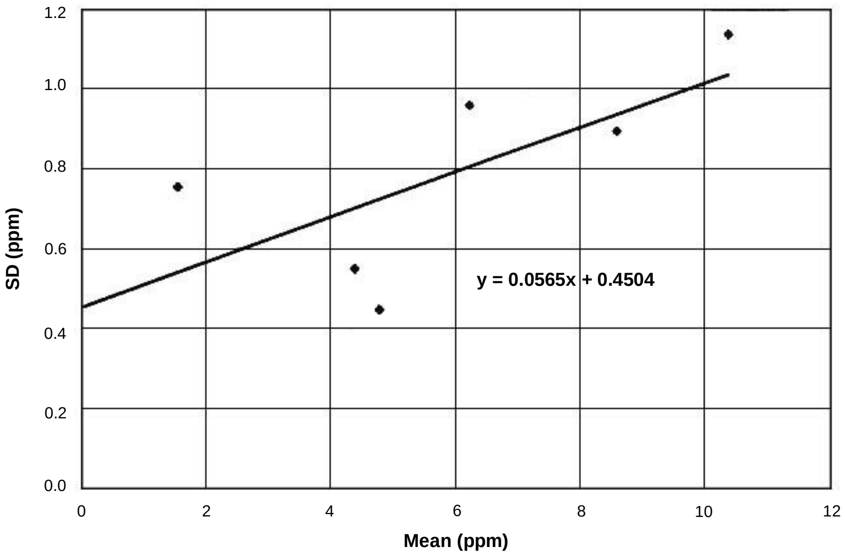
Samples	Mean	SD
STANDARD 1	48.00	1.0000
STANDARD 2	55.00	2.1213
STANDARD 3	51.80	1.4832
STANDARD 4	24.40	1.1402
STANDARD 5	40.00	1.0000
STANDARD 6	03.75	0.5000
STANDARD 7	25.40	0.8944
J-1	08.71	1.2724
COR-1	15.14	1.8996
M-1	12.89	1.8326

Figure 9. Nickel. Regression of standard deviation on mean of replicate analyses of standard samples



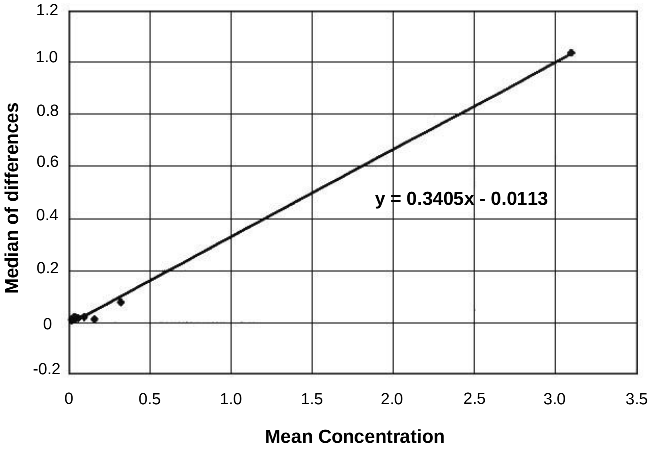
Mean	Median
1.68	2.34
2.14	1.00
2.64	1.00
3.26	2.00
22.18	1.00

Figure 10. Molybdenum. Regression of median of differences on mean of groups of duplicate analyses



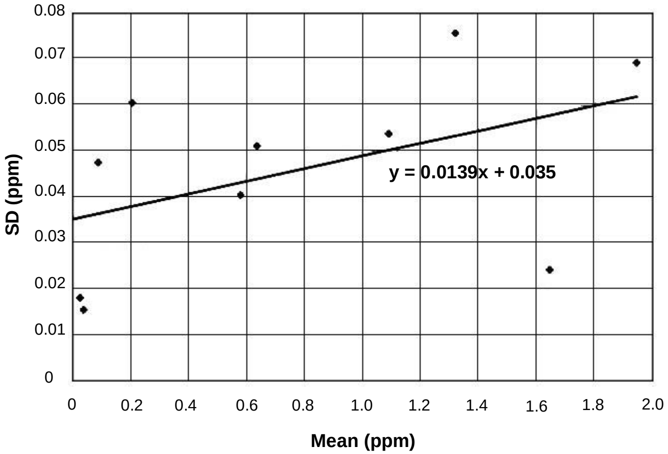
Samples	Mean	SD
STANDARD 1	10.40	1.1402
STANDARD 3	4.40	0.5477
STANDARD 4	4.80	0.4472
STANDARD 5	8.60	0.8944
STANDARD 6	6.25	0.9574
J-1	1.55	0.7507

Figure 11. Molybdenum. Regression of standard deviation on mean of replicate analyses of standard samples



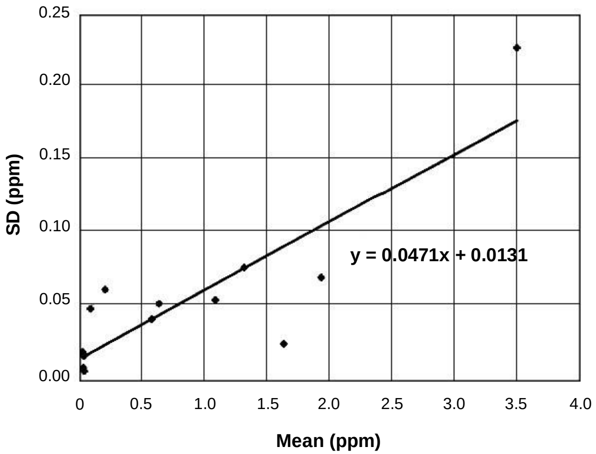
Mean	Median
0.0153	0.0074
0.0278	0.0160
0.0379	0.0170
0.0569	0.0140
0.0928	0.0180
0.1564	0.0100
0.3185	0.0750
3.0954	1.0460

Figure 12. Mercury. Regression of median of differences on mean of groups of duplicate analyses



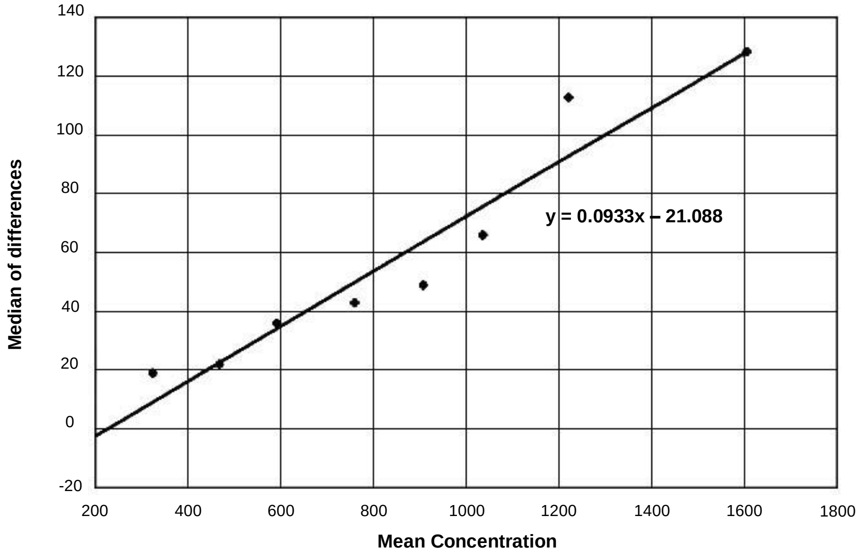
Samples	Mean	SD
STANDARD 1	1.3214	0.0757
STANDARD 2	1.9412	0.0693
STANDARD 3	1.6450	0.0244
STANDARD 4	0.5796	0.0404
STANDARD 5	1.0918	0.0537
STANDARD 6	0.2050	0.0601
STANDARD 7	0.6364	0.0509
J-1	0.0875	0.0473
COR-1	0.0260	0.0180
M-1	0.0384	0.0154

Figure 13. Mercury. Regression of standard deviation on mean of replicate analyses of standard samples



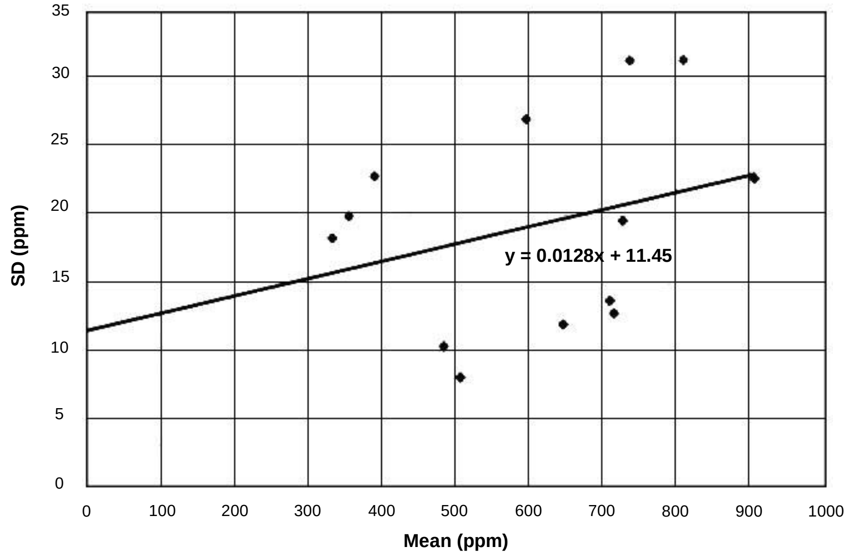
Samples	Mean	SD
STANDARD 1	1.3214	0.0757
STANDARD 2	1.9412	0.0693
STANDARD 3	1.6450	0.0244
STANDARD 4	0.5796	0.0404
STANDARD 5	1.0918	0.0537
STANDARD 6	0.2050	0.0601
STANDARD 7	0.6364	0.0509
J-1	0.0875	0.0473
COR-1	0.0260	0.0180
M-1	0.0384	0.0154
BCC3	3.501222	0.227508
BCC4	0.033000	0.007394
BCC5	0.041364	0.005104

Figure 14. Mercury. Regression of standard deviation on mean of replicate analyses of standard samples



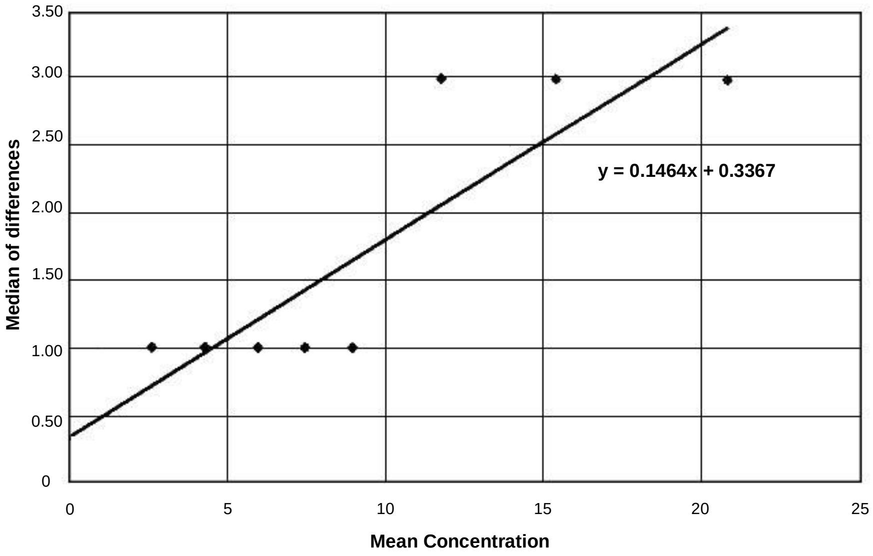
Mean	Median
324.27	19
468.05	22
590.96	36
760.14	43
909.50	49
1037.55	66
1222.59	113
1607.46	129

Figure 15. Manganese. Regression of median of differences on mean of groups of duplicate analyses



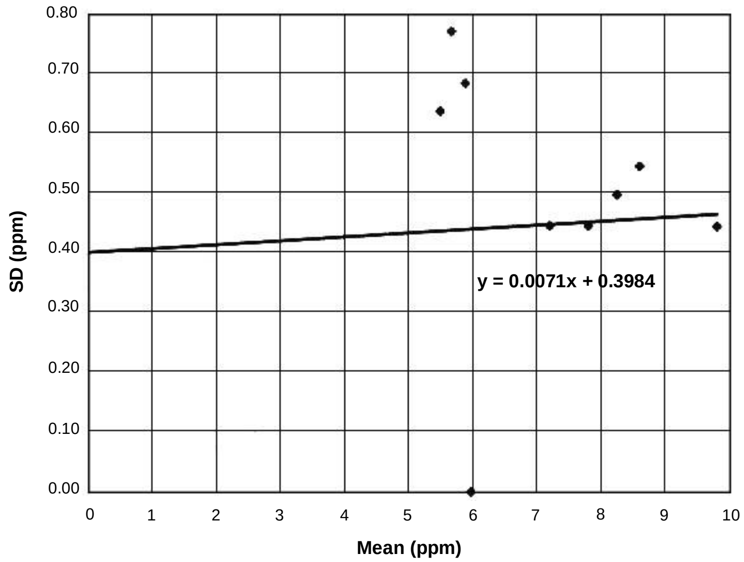
Samples	Mean	SD
STANDARD 1	727.20	19.6138
STANDARD 2	710.00	13.7477
STANDARD 3	715.60	12.8375
STANDARD 4	508.00	08.0932
STANDARD 5	647.00	12.0000
STANDARD 6	905.75	22.7211
STANDARD 7	485.20	10.3779
J-1	390.75	22.7867
COR-1	333.07	18.2552
M-1	355.82	19.8570
BCC3	809.80	31.50238
BCC4	596.90	27.04092
BCC5	737.1667	31.44644

Figure 16. Manganese. Regression of standard deviation on mean of replicate analyses of standard samples



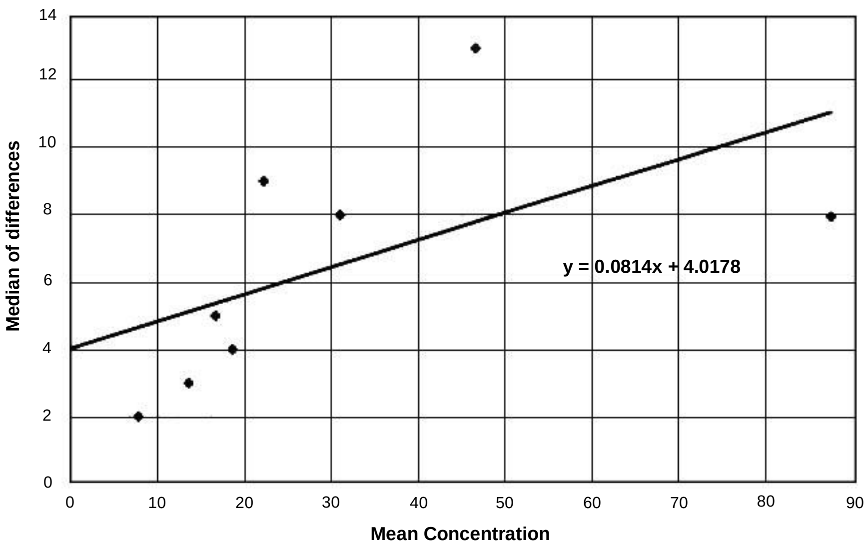
Mean	Median
2.591	1
4.273	1
5.955	1
7.455	1
8.955	1
11.773	3
15.409	3
20.818	3

Figure 17. Lithium. Regression of median of differences on mean of groups of duplicate analyses



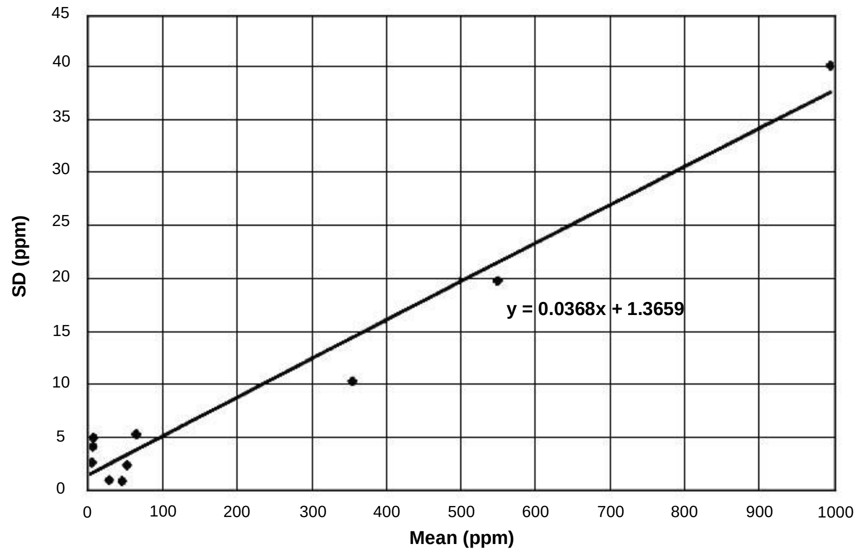
Samples	Mean	SD
STANDARD 1	9.80	0.447
STANDARD 2	6.00	0.000
STANDARD 3	7.80	0.447
STANDARD 4	7.20	0.447
STANDARD 5	8.60	0.548
STANDARD 6	8.25	0.500
STANDARD 7	6.00	0.000
J-1	5.89	0.685
COR-1	5.50	0.638
M-1	5.68	0.772

Figure 18. Lithium. Regression of standard deviation on mean of replicate analyses of standard samples



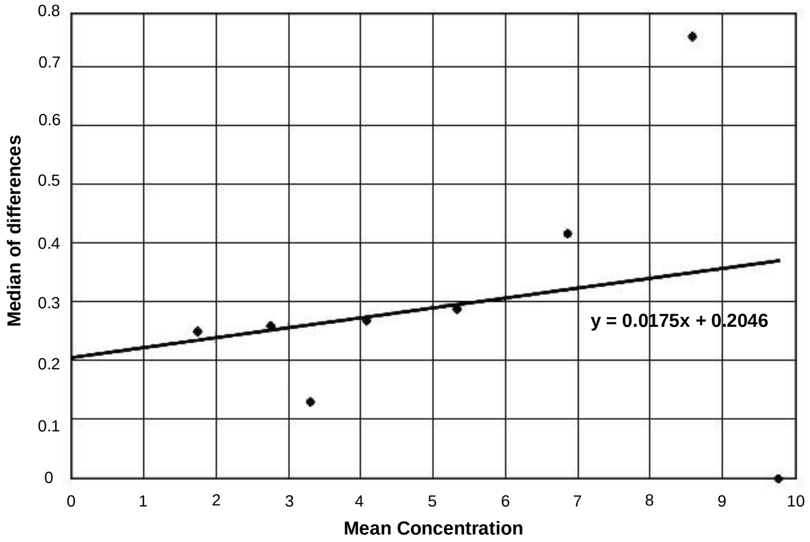
Mean	Median
7.82	2
13.59	3
16.68	5
18.64	4
22.18	9
31.00	8
46.68	13
87.32	8

Figure 19. Lead. Regression of median of differences on mean of groups of duplicate analyses



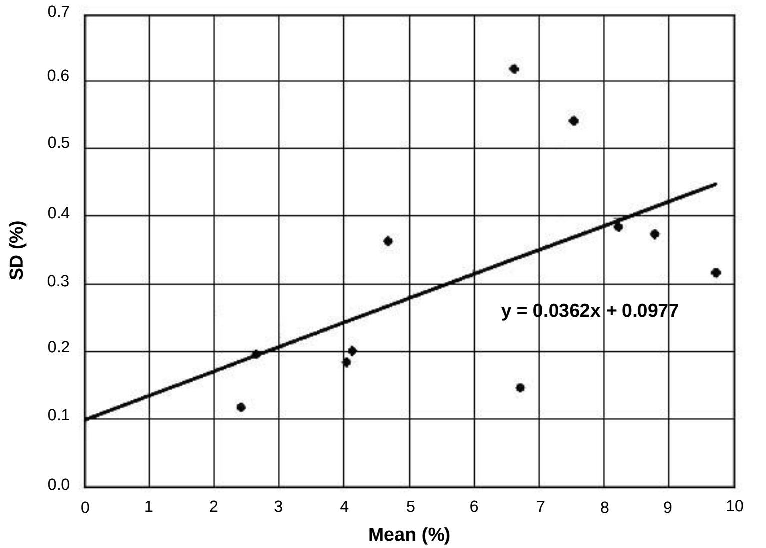
Samples	Mean	SD
STANDARD 1	64.60	5.2249
STANDARD 2	994.20	40.4747
STANDARD 3	550.00	19.8368
STANDARD 4	28.60	0.8944
STANDARD 5	52.60	2.3022
STANDARD 6	46.00	0.8165
STANDARD 7	355.60	10.3000
J-1	5.21	2.5540
COR-1	7.36	4.8805
M-1	6.69	4.0547

Figure 20. Lead. Regression of standard deviation on mean of replicate analyses of standard samples



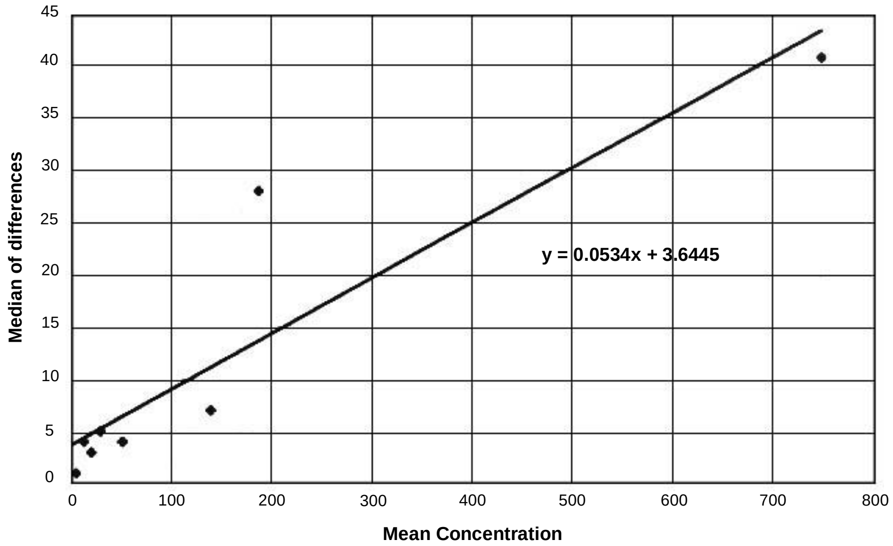
Mean	Median
1.75	0.25
2.76	0.26
3.32	0.13
4.09	0.27
5.34	0.29
6.86	0.42
8.59	0.76
9.78	0.00

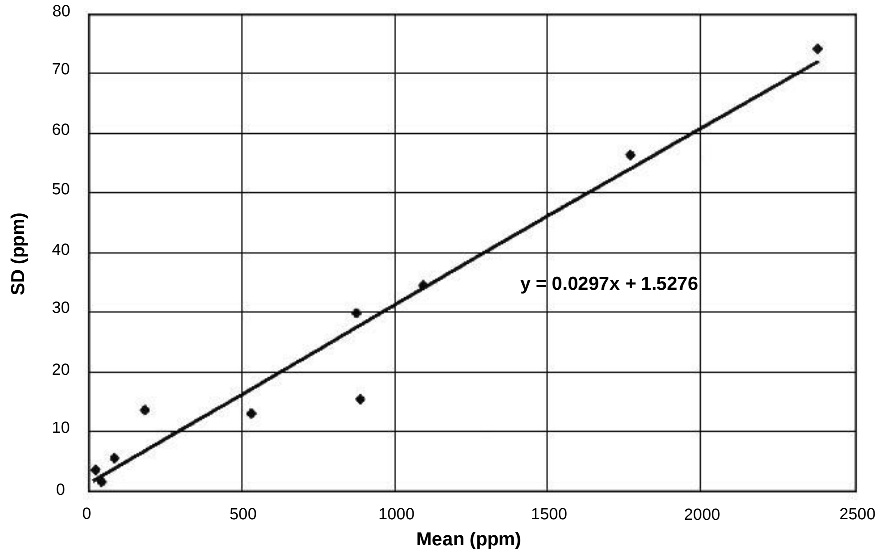
Figure 21. Iron. Regression of median of differences on mean of groups of duplicate analyses



Samples	Mean	SD
STANDARD 1	9.72	0.3182
STANDARD 4	6.72	0.1467
STANDARD 5	8.78	0.3757
STANDARD 6	2.65	0.1952
STANDARD 7	8.22	0.3861
J-1	4.68	0.3636
COR-1	7.54	0.5427
M-1	6.63	0.6191
BCC3	4.135	0.200458
BCC4	2.413	0.116909
BCC5	4.045	0.183872

Figure 22. Iron. Regression of standard deviation on mean of replicate analyses of standard samples



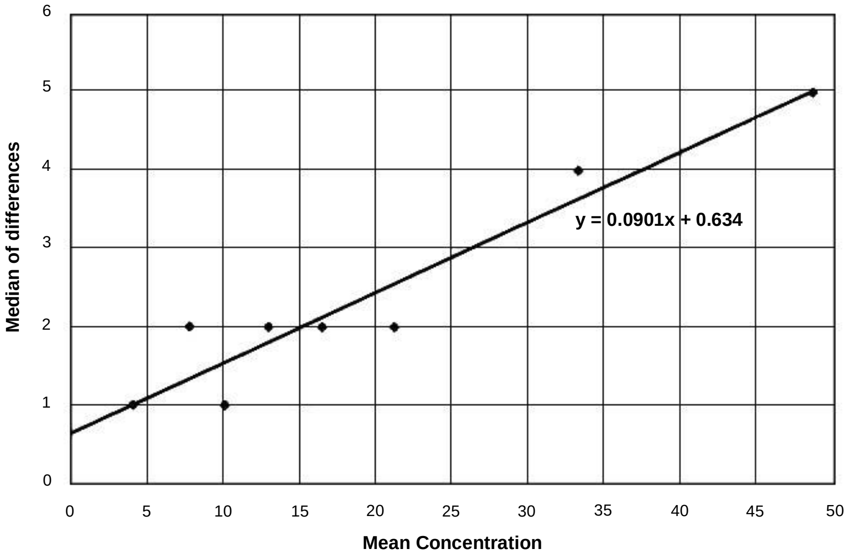


Mean	Median
5.48	1
13.27	4
20.73	3
29.91	5
51.86	4
139.73	7
186.91	28
747.77	41

Samples	Mean	SD
STANDARD 1	1093.80	34.4267
STANDARD 2	2380.40	74.2651
STANDARD 3	1768.80	56.3001
STANDARD 4	530.00	13.1719
STANDARD 5	888.40	15.5820
STANDARD 6	40.50	1.7321
STANDARD 7	875.00	29.8329
J-1	181.43	13.7368
COR-1	20.71	3.7303
M-1	82.43	5.6793

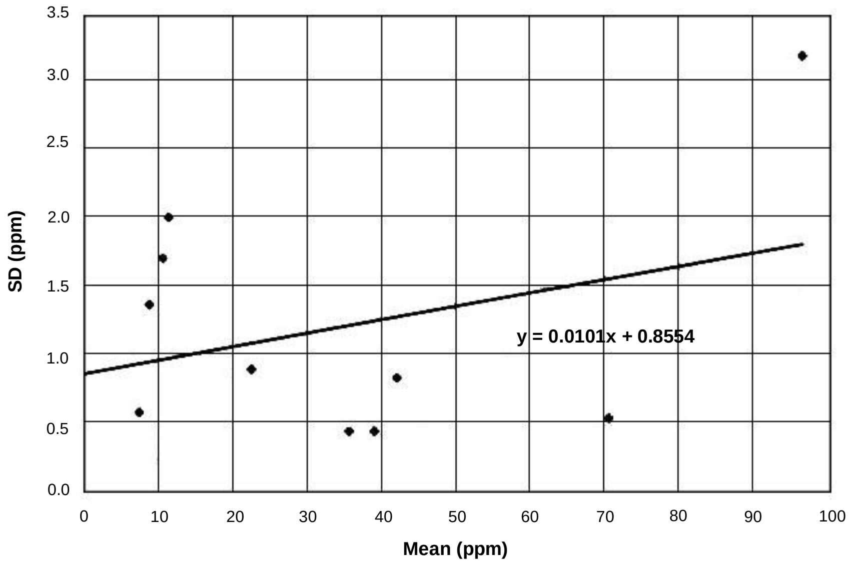
Figure 23. Copper. Regression of median of differences on mean of groups of duplicate analyses

Figure 24. Copper. Regression of standard deviation on mean of replicate analyses of standard samples



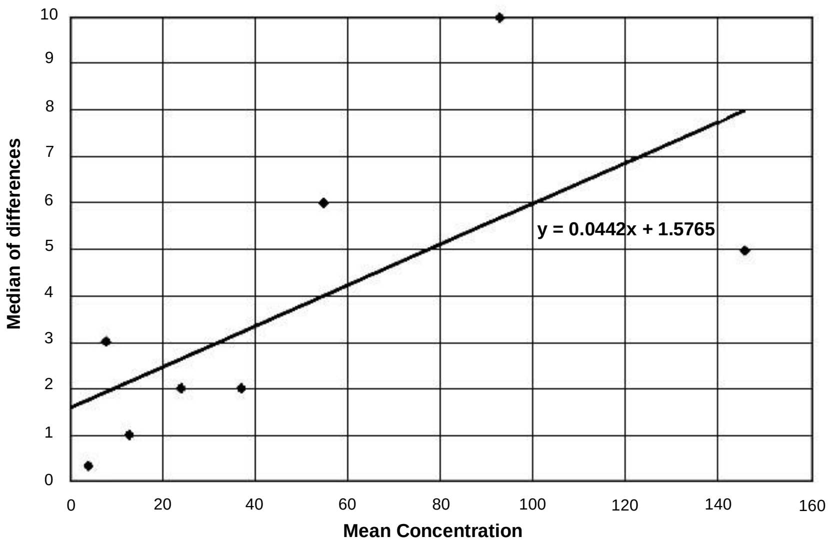
Mean	Median
4.08	1
7.77	2
10.09	1
12.96	2
16.50	2
21.27	2
33.32	4
48.64	5

Figure 25. Cobalt. Regression of median of differences on mean of groups of duplicate analyses



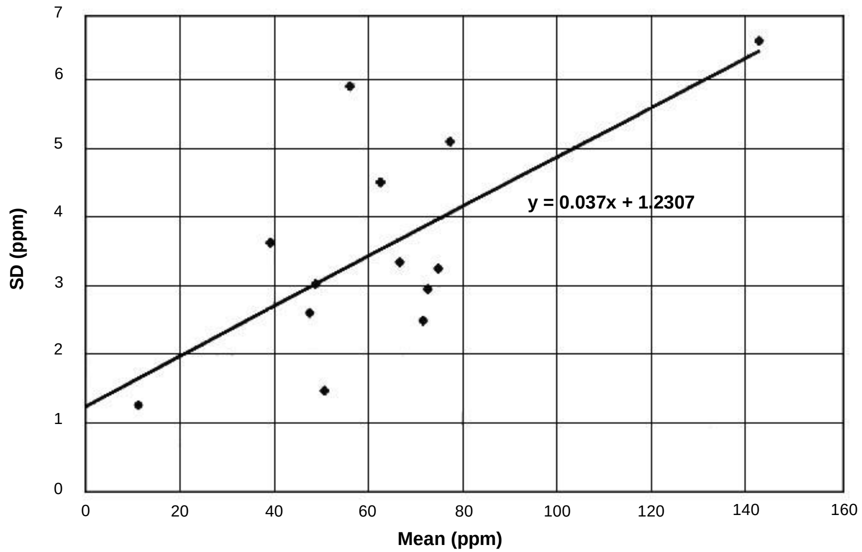
Samples	Mean	SD
STANDARD 1	42.20	0.8367
STANDARD 2	96.40	3.2094
STANDARD 3	70.60	0.5477
STANDARD 4	22.60	0.8944
STANDARD 5	35.80	0.4472
STANDARD 6	7.50	0.5774
STANDARD 7	39.20	0.4472
J-1	8.82	1.3623
COR-1	11.39	2.0063
M-1	10.64	1.7043

Figure 26. Cobalt. Regression of standard deviation on mean of replicate analyses of standard samples



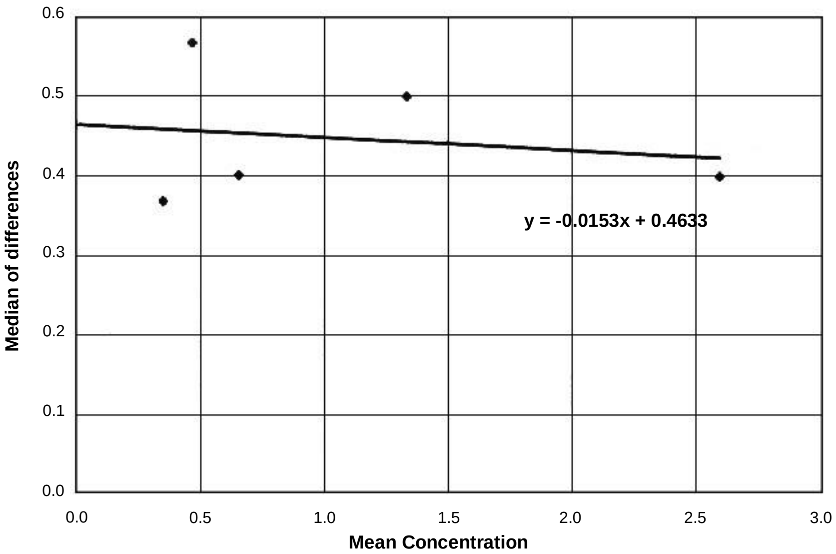
Mean	Median
3.85	0.34
7.64	3.00
12.64	1.00
23.86	2.00
36.86	2.00
54.68	6.00
93.00	10.00
145.59	5.00

Figure 27. Chromium. Regression of median of differences on mean of groups of duplicate analyses



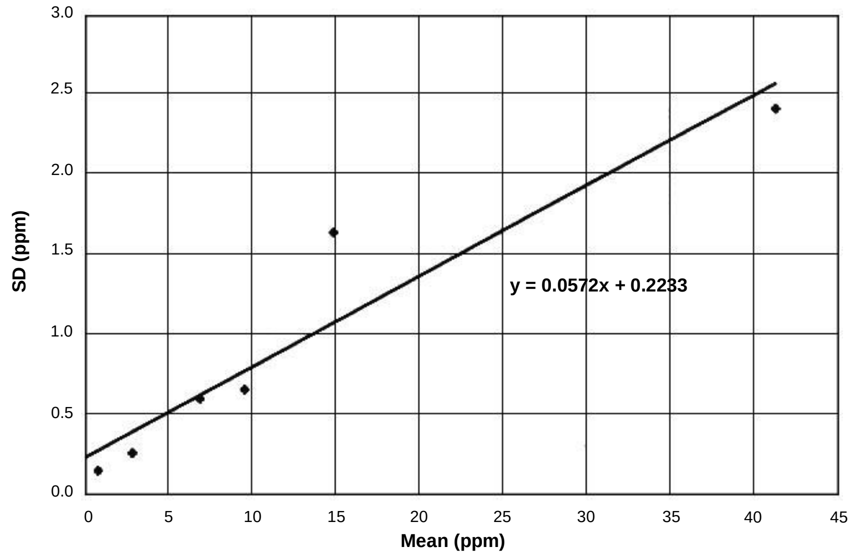
Samples	Mean	SD
STANDARD 1	74.80	3.2711
STANDARD 2	71.60	2.5100
STANDARD 3	72.60	2.9665
STANDARD 4	50.80	1.4832
STANDARD 5	66.60	3.3615
STANDARD 6	11.25	1.2583
STANDARD 7	48.80	3.0332
J-1	39.11	3.6346
COR-1	62.46	4.5337
M-1	55.96	5.9472
BCC3	142.4	6.65332
BCC4	77.2	5.138093
BCC5	47.5	2.611165

Figure 28. Chromium. Regression of standard deviation on mean of replicate analyses of standard samples



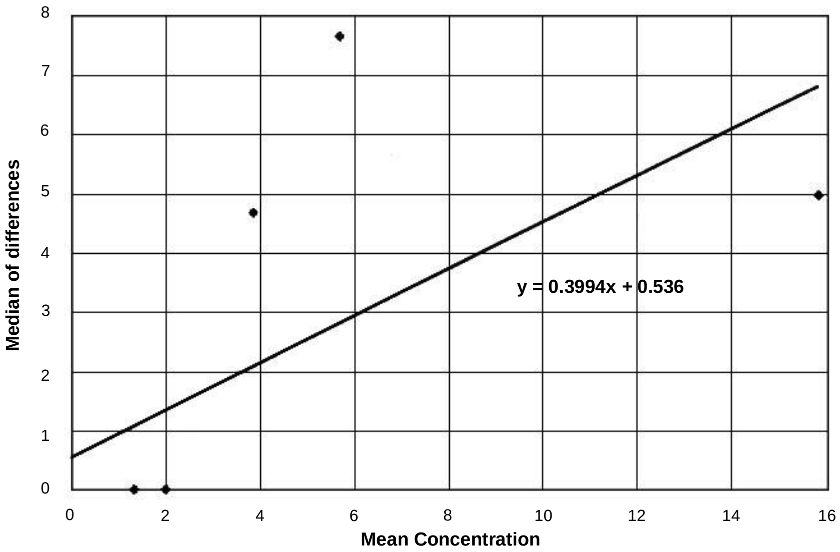
Mean	Median
0.350	0.367
0.468	0.567
0.655	0.400
1.336	0.500
2.595	0.400

Figure 29. Cadmium. Regression of median of differences on mean of groups of duplicate analyses



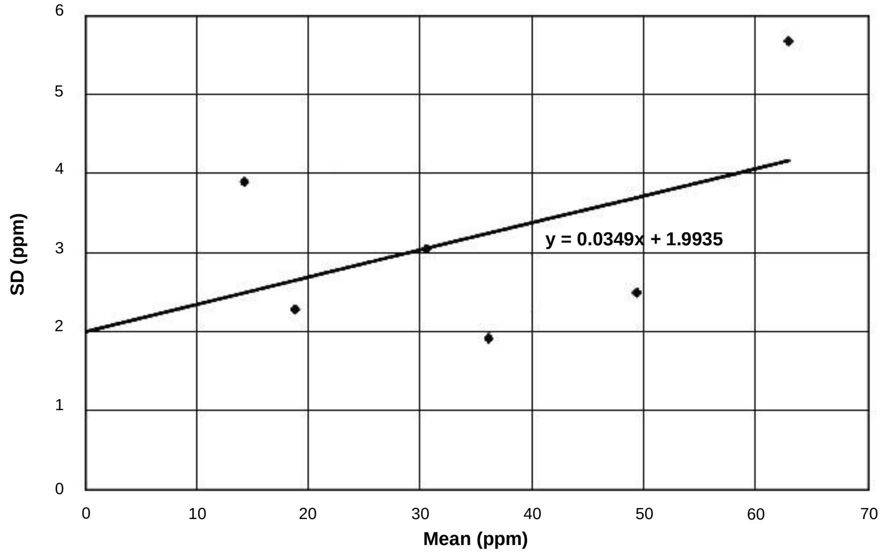
Samples	Mean	SD
STANDARD 1	9.58	0.6535
STANDARD 3	41.30	2.4238
STANDARD 4	2.84	0.2510
STANDARD 5	6.88	0.5933
STANDARD 6	0.80	0.1414
STANDARD 7	14.90	1.6386

Figure 30. Cadmium. Regression of standard deviation on mean of replicate analyses of standard samples



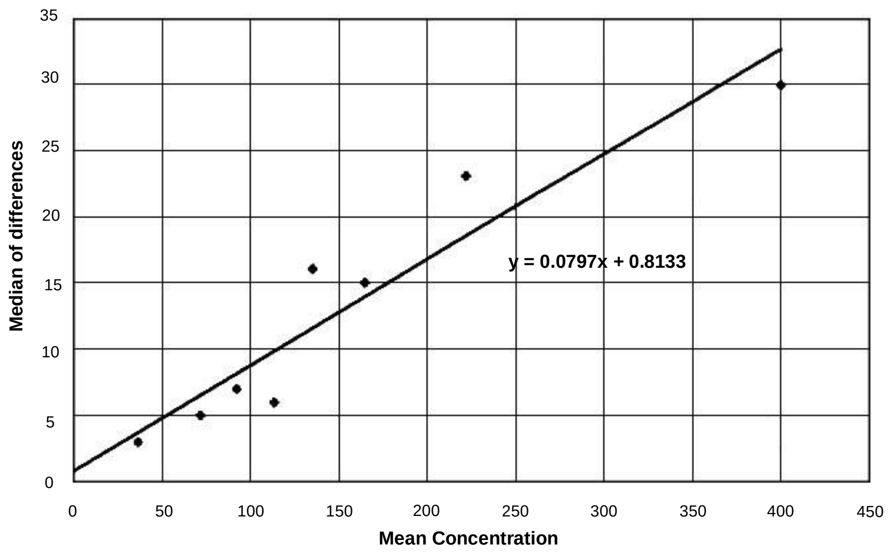
Mean	Median
1.330	0.00
1.330	0.00
1.330	0.00
1.330	0.00
1.997	0.00
3.847	4.67
5.695	7.67
15.818	5.00

Figure 31. Bismuth. Regression of median of differences on mean of groups of duplicate analyses



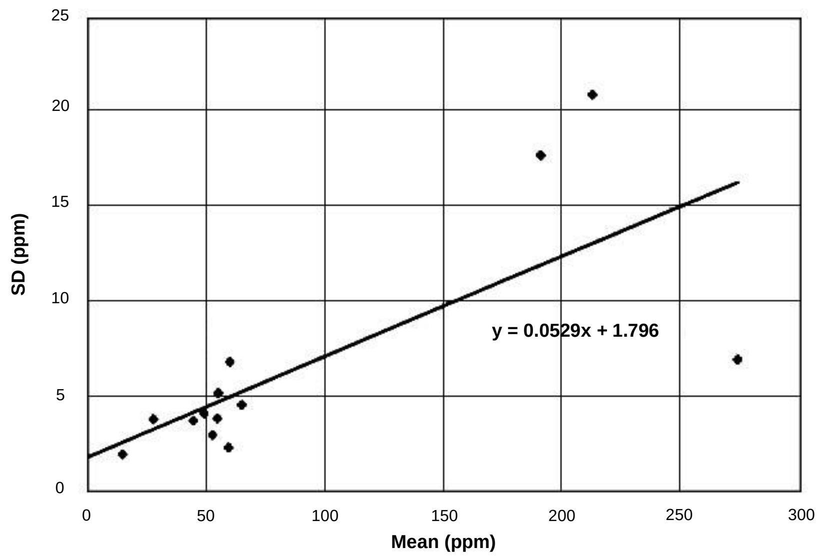
Samples	Mean	SD
STANDARD 1	36.20	1.9235
STANDARD 2	63.00	5.7009
STANDARD 3	49.40	2.5100
STANDARD 4	14.20	3.8987
STANDARD 5	30.60	3.0496
STANDARD 7	18.80	2.2804

Figure 32. Bismuth. Regression of standard deviation on mean of replicate analyses of standard samples



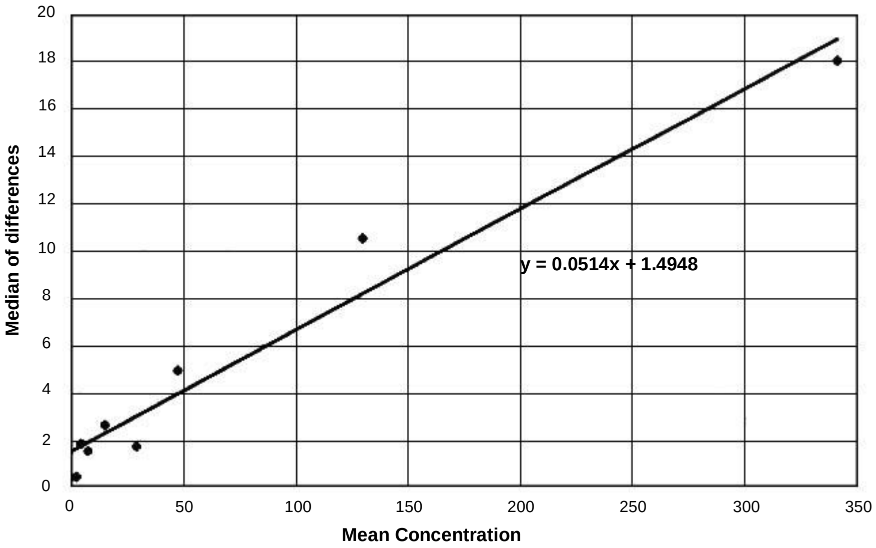
Mean	Median
36.27	3
71.60	5
92.05	7
113.36	6
135.05	16
164.77	15
222.18	23
400.18	30

Figure 33. Barium. Regression of median of differences on mean of groups of duplicate analyses



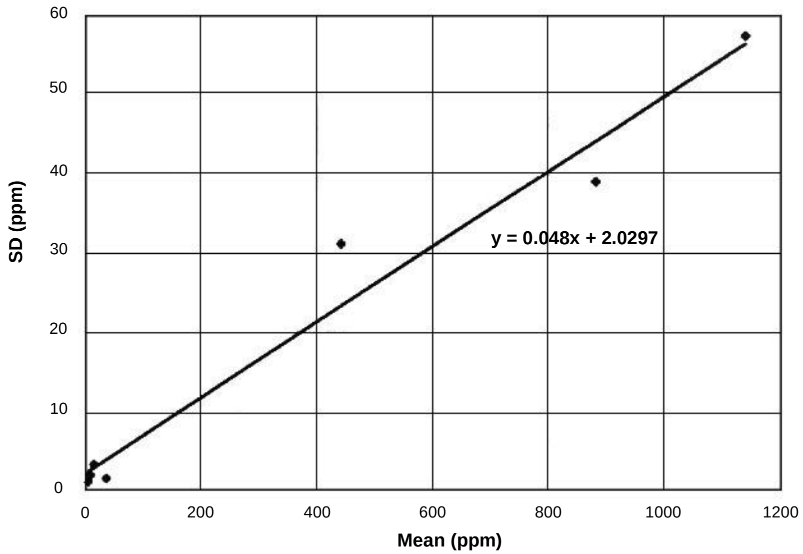
Samples	Mean	SD
STANDARD 1	52.60	2.9665
STANDARD 2	14.60	1.9494
STANDARD 3	27.60	3.7815
STANDARD 4	59.40	2.3022
STANDARD 5	54.60	3.8471
STANDARD 6	274.25	6.9940
STANDARD 7	44.40	3.7148
J-1	65.00	4.5461
COR-1	48.93	4.0818
M-1	54.96	5.1674
BCC3	213	20.96028
BCC4	59.9	6.789698
BCC5	191.25	17.69502

Figure 34. Barium. Regression of standard deviation on mean of replicate analyses of standard samples



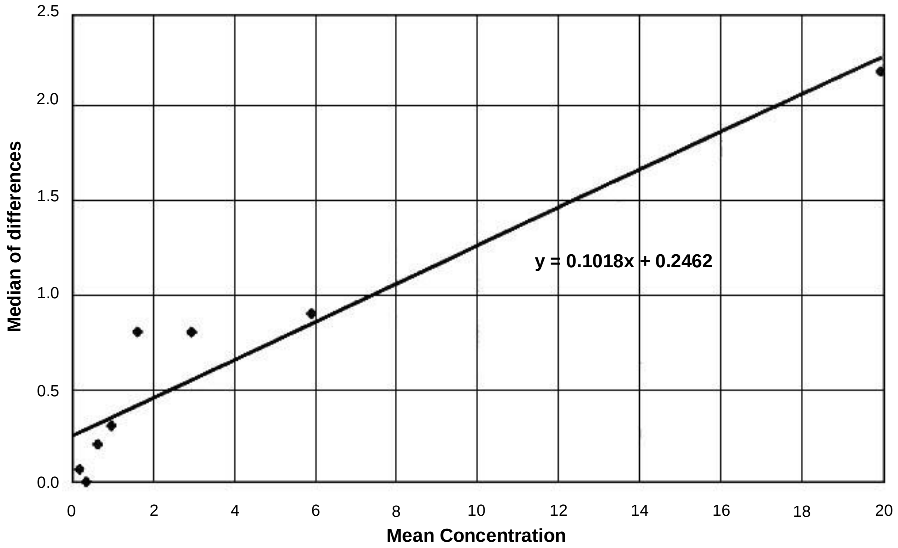
Mean	Median
2.03	0.4
4.19	1.8
7.22	1.5
14.74	2.6
28.84	1.7
47.20	4.9
129.70	10.5
341.11	18.1

Figure 35. Arsenic. Regression of median of differences on mean of groups of duplicate analyses



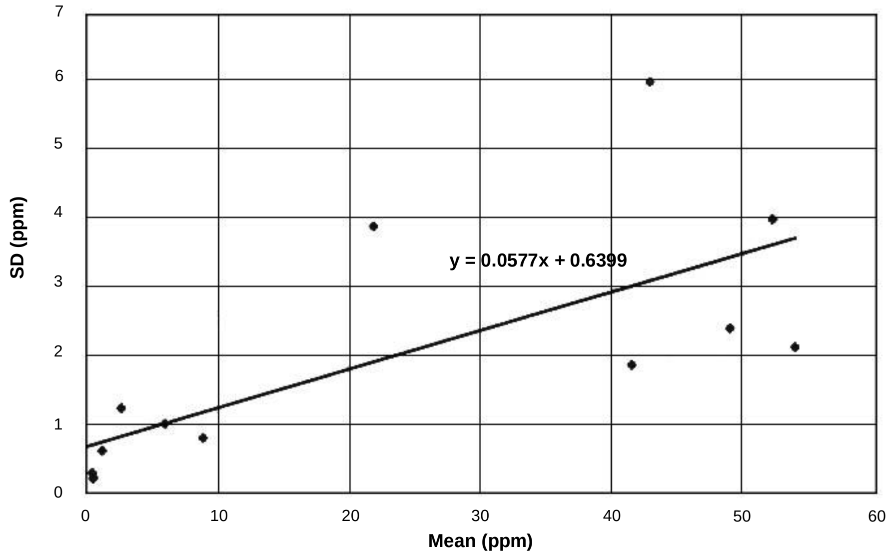
Samples	Mean	SD
STANDARD 1	1137.56	57.57
STANDARD 4	441.64	31.04
STANDARD 5	879.56	39.10
STANDARD 6	36.75	1.45
J-1	14.92	3.20
COR-1	5.15	1.06
M-1	9.08	1.86

Figure 36. Arsenic by AAS. Regression of standard deviation on mean of replicate analyses of standard samples



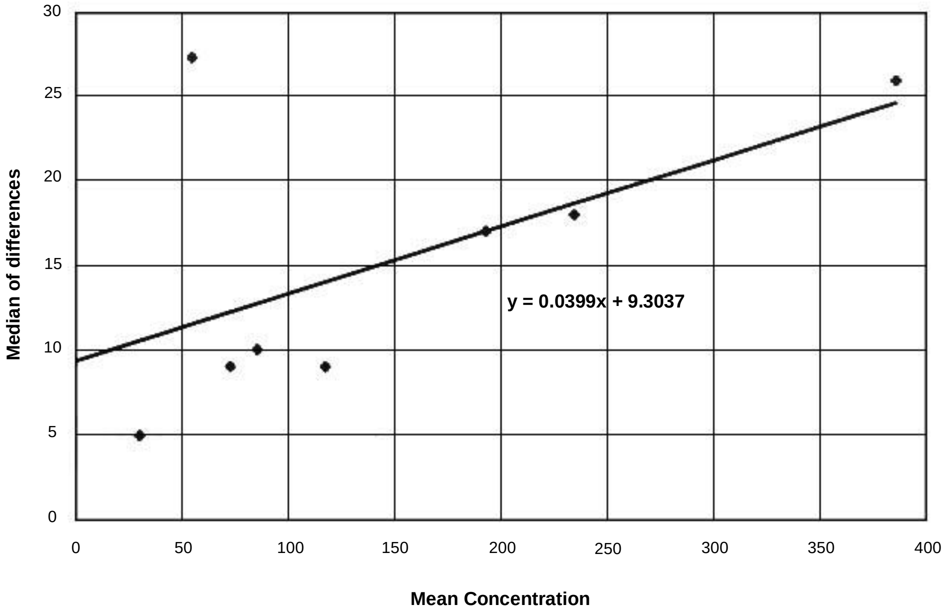
Mean	Median
0.165	0.067
0.336	0.000
0.611	0.200
0.955	0.300
1.591	0.800
2.927	0.800
5.895	0.900
19.905	2.200

Figure 37. Antimony. Regression of median of differences on mean of groups of duplicate analyses



Samples	Mean	SD
STANDARD 1	52.180	4.0258
STANDARD 2	53.920	2.1569
STANDARD 3	49.020	2.4294
STANDARD 4	21.900	3.8839
STANDARD 5	41.560	1.8823
STANDARD 6	6.000	0.9832
STANDARD 7	8.900	0.7778
J-1	2.646	1.2057
COR-1	0.439	0.2583
M-1	1.215	0.5832
BCC3	42.91111	6.032919
BCC4	0.510000	0.172884
BCC5	0.563636	0.185864

Figure 38. Antimony by AAS. Regression of standard deviation on mean of replicate analyses of standard samples



Mean	Median
30.09	5.0
54.86	27.3
72.68	9.0
85.36	10.0
117.55	9.0
193.23	17.0
234.72	18.0
385.50	26.0

Figure 39. Vanadium. Regression of median of differences on mean of groups of duplicate analyses